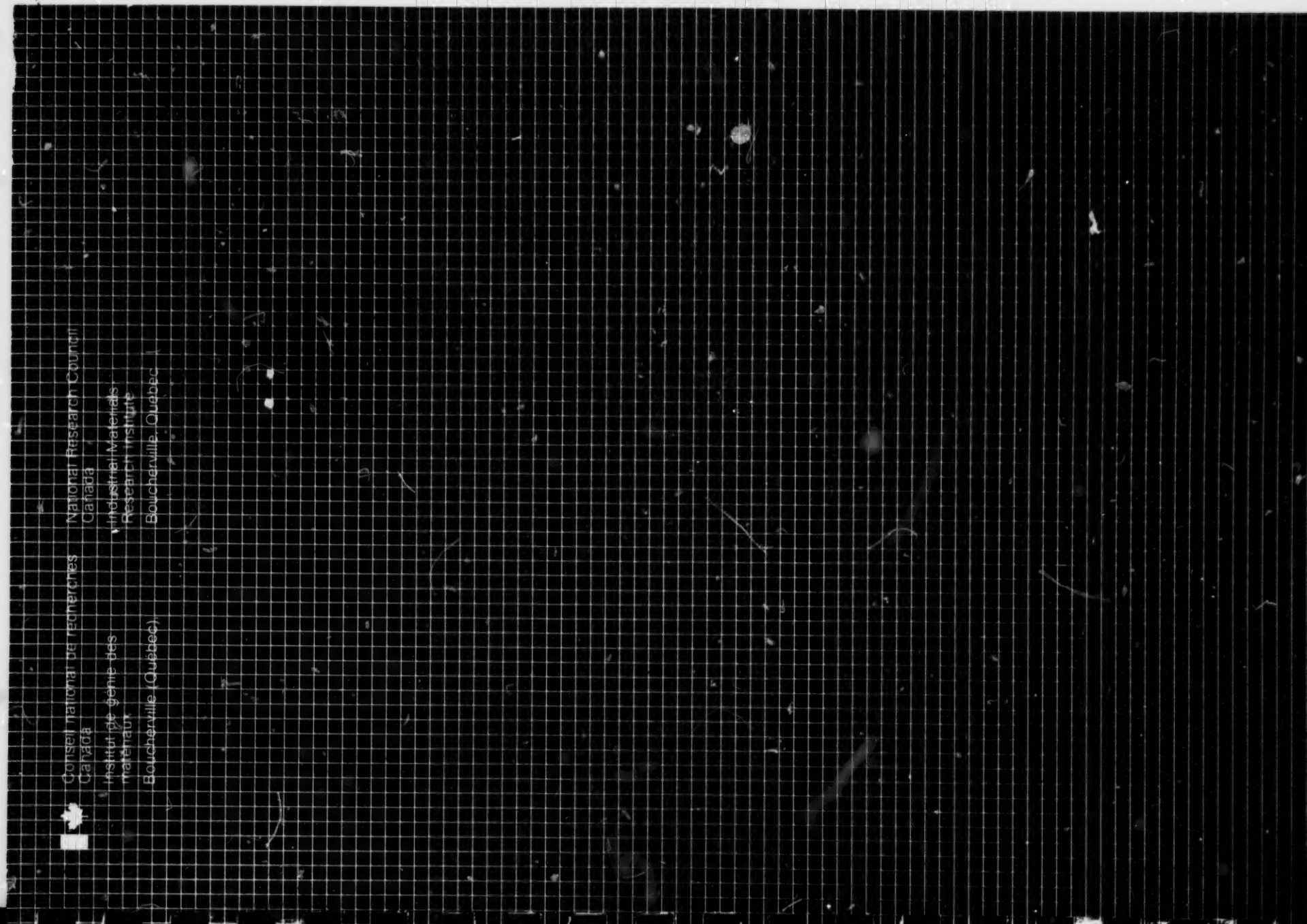
PHYSICOCHEMICAL CHARACTERIZATION OF HIGH-PERFORMANCE FIBRE-REINFORCED ORGANIC-MATRIX COMPOSITES
Part 5. STUDY OF THE ROOM-TEMPERATURE AGING OF NARMCO 5208/MC3000 PREPREG



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PHYSICOCHEMICAL CHARACTERIZATION OF HIGH-PERFORMANCE FIBRE-REINFORCED ORGANIC-MATRIX COMPOSITES

PART 5. A STUDY OF THE ROOM-TEMPERATURE AGING OF NARMCO 5208/WC3000 PREPREG

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PREFACE

This report is the fifth of a series resulting from a cooperative effort involving the Industrial Materials Research Institute (IMRI) of the National Research Council Canada (NRCC) (Boucherville, Québec) and Canadair Limited (Montréal, Québec). The subject is one of growing importance in high-technology manufacturing, namely the physicochemical characterization of high-performance fibre-reinforced organic-matrix composites. This report describes the application of a number of physicochemical and mechanical testing methods to a study of the room-temperature aging of Narmco Rigidite 5208/WC3000 graphite-epoxy prepreg. Other reports in the series include a general discussion and literature review, as well as reports on the development of the analytical techniques used in this study. The titles of the complete series are as follows:

Part 1. General Discussion and Literature Review
Part 2. Applications of Infrared Spectroscopy
Part 3. Applications of Liquid Chromatography
Part 4. Applications of Pyrolysis Gas Chromatography and Thermal Analysis
Part 5. A Study of the Room-Temperature Aging of Narmco 5208/WC3000 Prepreg
Part 6. Methods for Quality Control of Matrix Chemistry

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SUMMARY

The report describes a study of the changes which occur in Narmco Rigidite 5208/WC3000 carbon-epoxy prepreg when it is exposed to ambient temperature (22°C) and 50% relative humidity. The organic matrix in this system consists of a reactive mixture containing epoxy resin (primarily tetraglycidyldiaminodiphenylmethane, or TGDDM) and an amine hardener (diaminodiphenylsulphone, or DDS). When it is subjected to ambient temperatures, gradual polymerization takes place. Samples exposed for different periods of time up to 66 days were analysed in depth using various techniques to determine the extent of the chemical changes occurring and their effect on the physical properties. In addition, cured panels made from the aged prepreg were tested to see whether their mechanical properties were affected by the aging.

The physicochemical techniques used were Fourier transform infrared spectroscopy (transmission, attenuated total reflection, and diffuse reflection), liquid chromatography (reverse-phase, high-speed reverse-phase, and high-performance size-exclusion), thermal analysis (differential scanning calorimetry and thermogravimetric analysis), and pyrolysis - capillary gas chromatography. These have been described in previous reports in the series. All showed evidence of significant changes, the most sensitive being Fourier transform infrared (FTIR) and reverse-phase liquid chromatography (RPLC). FTIR showed that the number of unreacted epoxy groups decreases steadily at a rate of 0.34% per day, based on the initial amount. At the same time, the number of free DDS molecules, as monitored by RPLC, drops at a rate of 1.02% per day. RPLC also showed that the amount of TGDDM-DDS reaction product increases significantly over the first thirty days but then declines as it undergoes further reaction to give higher-molecular-weight products. The heat of polymerization of the resin, measured by thermal analysis, decreased by 0.26% per day from its initial value of 561 J/g.

Of the physical properties, the gel time was the most affected by the aging. Over the 66-day period, it dropped from 21 minutes to 7 minutes. The volatiles content, initially at 1.9%, decreased substantially over the first few days, then levelled off at 0.8%. The decrease was found to be due to loss of acetone and was accompanied by a notable loss of tack. The resin flow showed no significant change.

The mechanical testing results showed considerable scatter. No correlation was observed between tensile properties and prepreg aging. However, the compressive properties and short beam shear strength showed evidence of a slight downward trend (about 0.2% to 0.4% per day of prepreg exposure). Although this effect is small, it could well be much more important for complex parts made in a factory environment under less ideal conditions.

A sample exposed for 50 days at 22°C but under a dry atmosphere was also studied. The changes observed were of about the same magnitude as those seen in the sample exposed for 35 days at 50% R.H. In contrast, a sample stored in a freezer at -25°C for 87 days showed no detectable changes.

RÉSUMÉ

Ce rapport décrit les variations physicochimiques subies par le pré-imprégné carbone-époxyde Narmco Rigidite 5208/WC3000 lors d'une exposition à temperature ambiante (22°C) et à 50% d'humidité relative. La matrice organique dans ce système est constituée d'un mélange réactif comprenant une résine époxyde (principalement le tétraglycidyl-diaminodiphénylméthane, ou TGDDM) et un durcisseur amine (le diaminodiphénylsulfone, ou DDS). Ce mélange polymérise graduellement lorsqu'il est maintenu à la température ambiante. Des échantillons exposés pour différentes périodes jusqu'à 66 jours ont été analysés à l'aide de différentes techniques. En plus, des panneaux durcis fabriqués à partir du pré-imprégné vieilli ont été analysés pour déterminer les effets sur les propriétés mécaniques.

Les techniques physicochimiques incluaient la spectroscopie infrarouge à transformée de Fourier (transmission, réflexion totale atténuée, réflexion diffuse), la chromatographie liquide (phase inversée, phase inversée à haute vitesse, exclusion haute performance), l'analyse thermique (calorimétrie différentielle à balayage, thermogravimétrie), et la pyrolyse - chromatographie en phase gazeuse sur colonne capillaire. Ces techniques ont été décrites dans les rapports précédents. Elles montrent toutes un changement significatif de la résine époxyde, mais la spectroscopie infrarouge (SIRTF) et la chromatographie liquide en phase inversée (CLPI) sont les plus sensibles. La SIRTF montre une diminution continuelle du nombre de groupements époxydes libres à un taux de 0.34% par jour. Durant la même période, une baisse de 1.02% par jour du nombre de molécules libres de DDS est enregistrée par CLPI. La chromatographie indique aussi une augmentation du produit de réaction TGDDM-DDS durant les premiers 30 jours, suivie d'une diminution lors de la formation de produits de poids moléculaires élevés. L'enthalpie de polymérisation, mesurée par l'analyse thermique, décroît de 0.26% par jour à partir de sa valeur initiale de 561 J/g.

Parmi les propriétés physiques, le temps de gel est le plus affecté par le vieillissement. Sur une période de 66 jours, il décroît de 21 à 7 minutes. Le pourcentage de produits volatiles, initialement à 1.9%, diminue substantiellement durant les premiers jours et par la suite, il se maintient à 0.8%. La baisse est attribuée à la perte d'acétone et s'accompagne d'une perte du caractère collant ("tack"). L'écoulement de la résine ne montre pas de changements significatifs.

Les tests mécaniques montrent une dispersion importante. Il n'existe pas de corrélation entre les propriétés de traction et le vieillissement du pré-imprégné. Cependant, les propriétés de compression et la résistance au cisaillement interlaminaire indiquent une faible tendance à la baisse (0.2% à 0.4% par jour de viellissement). Ces effets pourraient être plus importants pour des pièces complexes fabriquées en usine dans des conditions moins idéales.

Un échantillon exposé durant 50 jours à 22°C sous atmosphère sèche montre des changements similaires à un échantillon exposé 35 jours à 50% d'humidité relative. À l'opposé, un échantillon exposé 87 jours à -25°C ne montre aucun changement.

1. INTRODUCTION

This report is the fifth of a series concerned with the application of physicochemical testing methods to high-performance composite materials consisting of high-strength reinforcing fibres (glass, carbon, Kevlar®) embedded in an organic polymer matrix (epoxy, polyimide, or polyester). As outlined in the first report [1], the objective of the research project was to develop improved methods for the rapid and accurate characterization of the chemical composition of the organic matrix materials. Such methods are becoming more common in quality control laboratories as the applications of composite materials grow, particularly in the aerospace industry. The first report also gives a general discussion of the subject and a comprehensive review of the recent literature including some 300 references.

The second, third, and fourth reports of the series [2,3,4] describe the development of specific analytical methods using various techniques, namely infrared spectroscopy (IR), liquid chromatography (LC), thermal analysis, and pyrolysis - capillary gas chromatography (PGC).

The present report describes the application of these methods to a particular problem — the aging of graphite-epoxy prepreg. Such a prepreg contains a reactive mixture of epoxy resin and hardener. To prevent premature reaction which could render it unusable, it must be stored at low temperature and protected from humidity. Otherwise, the chemical reactions which occur (referred to as "resin advancement") will change the physical properties and processing behaviour of the system. This in turn can affect the mechanical performance of parts made from the prepreg, especially in the long term. It is thus important to have reliable methods for checking the degree of advancement of the prepreg to ensure that it has not been exposed to adverse conditions.

The work described herein involves a comprehensive study of one particular prepreg (Narmco Rigidite 5208/WC3000) when exposed to room temperature and 50% relative humidity over a period of 66 days. The aims of the work were threefold: (i) to determine the magnitude of the changes which occur, not only in terms of chemical composition but also in terms of physical and mechanical properties; (ii) to compare the sensitivity of the different analytical methods for detecting these changes; and (iii) to establish correlations between physical, chemical, and mechanical properties.

The main components of the Narmco 5208 system are an epoxy resin based on tetraglycidyldiaminodiphenylmethane (TGDDM), and the amine hardener diaminodiphenylsulphone (DDS). There is also a small amount of a second epoxy resin derived from a bisphenol A Novolac. Several other commercial systems (for example, Hercules

3501 and Fiberite 976) are also based on TGDDM and DDS but contain different minor components. Further details are given in an earlier report [1].

Some data have already been reported concerning the aging of such systems. Crabtree and Hewitt [5] followed the aging of TGDDM-DDS mixtures using reverse-phase high-performance liquid chromatography (HPLC) and size-exclusion chromatography (SEC). They observed a slight change after 46 days at 22°C and a substantial change after one year. At 0°C the changes were negligible, even after three years. Cured parts made from the latter material had the same strength as those made from fresh material. A later paper from the same group [6] reports more quantitative results for the commercial products Narmco 5208 and Hercules 3501. The ratio of certain peaks in the SEC chromatogram varies linearly with aging time. In the case of Hercules 3501, a similar trend was found for the ratio of peak heights in the differential scanning calorimetry (DSC) curve. Narmco 5208 gives only one DSC peak, so this analysis could not be applied.

Hinrichs and Thuen [7] studied Narmco 5208 using HPLC, moisture analysis, and rheological measurements. When prepreg is exposed to 50% or higher relative humidity, the moisture reaches a saturation level of about 0.7% in 5 hours. If the humidity level is less than 35%, the prepreg loses moisture to a limiting level of about 0.1%, also in 5 hours. HPLC could detect no changes in prepreg exposed 5 days at room temperature and 0% or 98% R.H. A high moisture content was found to increase the tackiness, to affect the viscosity profile during cure, and to produce porosity in the laminate. Fortunately, the moisture effects were found to be reversible. After humidity-exposed prepreg was dried in a desiccator, it behaved in the same way as it did before moisture absorption. The viscosity profile during cure was also found to be highly dependent on the degree of advancement, or B–staging, of the resin.

Lawless [8] used dynamic dielectric analysis (DDA) to study the aging of Narmco 5208 and Hercules 3501. A typical DDA curve plots the dissipation factor or loss tangent tan δ versus time as the sample is subjected to a controlled temperature program. Resin systems such as the ones mentioned usually show two peaks related to molecular mobility. The first, known as the "flow" peak, corresponds to a drop in viscosity which occurs when the resin is first heated. The second, or "gel" peak, corresponds to the point at which the resin is crosslinked to the extent of forming a three-dimensional network or "gel". In a resin system with a high degree of advancement, these two peaks occur closer together and may even merge. Lawless exposed prepreg at room temperature in both dry (0% R.H.) and wet (100% R.H.) conditions. In both cases, the Narmco prepreg became noticeably more rigid, or "boardy", after 2-3 weeks. After 6 weeks, both Narmco and Hercules prepregs lost essentially all tack and flow properties as compared to unexposed material. The DDA curves showed changes even after one day. Initially, the absorption of moisture has a plasticizing effect and moves the flow peak to lower temperature. After 1-2 weeks,

resin advancement begins to dominate. The DDA curve begins to show distortion and after 6 weeks the flow peak has disappeared completely, but the cure peak remains. Similar results have been reported by May [9] for TGDDM-DDS mixtures.

Sanjana [10] studied the aging of Hercules 3501 prepreg under the following conditions: ambient (26°C & 62% R.H.), 49°C dry, 49°C & 95% R.H., 49°C & 80% R.H. intermittent. Changes were easily detected by DDA and DMA (dynamic mechanical analysis) but not by DSC. The first noticeable physical change was loss of tack and drapability, which was considered to render the prepreg unusable. This occurred in two days at 49°C and in 3-4 weeks under ambient conditions. Laminate mechanical properties did not deteriorate until well beyond this point. The DMA curve measured for prepreg shows an initial damping peak associated with softening and flow of the resin, and the temperature at which this peak occurs increases linearly with the aging time. The same is true for the flow peak observed in DDA. Measurements of resin flow showed a corresponding gradual decrease. All these changes were correlated with readings given by a Time/Temperature Watch (TTW). This is a commercial device which indicates by a colour change the extent to which a material has been exposed to unfavourably high temperatures.

Hagnauer has also studied the aging of Hercules 3501 [11, 12] using SEC and normal-phase HPLC to determine the amounts of unreacted TGDDM monomer and DDS. He concluded that the prepreg becomes unacceptable for processing when these amounts drop from their initial values of 40% and 24% respectively to 28% and 16%. At 49°C this happens in two days, at 22° it takes over two weeks, and at -13° the prepreg is still good after one year. At 22° the drop in TGDDM and DDS is more rapid during the first week.

May [13] reports an HPLC analysis of a TGDDM-DDS formulation in which TGDDM and DDS were monitored as a function of aging time. The amounts decreased from 51% and 30% respectively to 44% and 22% over a period of 63 days. Similarly, Sewell [14] found that for Hercules 3501 after 40 days under dry ambient-temperature conditions the content of free DDS decreased by 35% and the amount of Novolac epoxy by 40%. Scola [15] used reverse-phase HPLC and IR (infrared spectroscopy) to follow the aging of Hercules 3501 prepreg for up to 14 days at 25°C and relative humidities of 0, 31, 51, and 93%. He found that the prepreg absorbed about twice as much moisture from the atmosphere as did the neat resin. The BF_3-amine catalyst present in this system has a particularly high affinity for moisture. In HPLC the ratio of the TGDDM peak to the reaction product peak was found to decrease with aging time, the rate being higher at higher humidity levels. (The term "reaction product" refers here and throughout this report to the molecule formed by reaction of one molecule of TGDDM with one molecule of DDS.) In IR the ratio of the epoxy peak at 910 cm^{-1} to the aromatic band at 1605 cm^{-1} was used as a measure of the amount of unreacted epoxy. The results were difficult to interpret because

of substantial scatter. Physical and mechanical properties (void content, compressive strength, interlaminar shear strength) did not appear to be adversely affected by the aging.

Pearce et al. [16,17] have studied the effect of moisture exposure (60°C, 96% R.H.) on neat epoxy resins, including some based on TGDDM. In this case, the moisture reacts with one epoxy group of the molecule to form an α-glycol. The rate of formation was measured by HPLC and was found to be higher for the commercial products than for pure TGDDM.

Larsson and Wirsén [18] studied the effects of freezer storage at -25 to -30°C on American Cyanamid prepreg BP-927 over a period of seven years. Although the hardener in this system is the same as in Narmco 5208 (DDS), the epoxies are different (TGPAP, or triglycidyl-p-aminophenol, and brominated diglycidyl ether of bisphenol A). They found no significant change in most properties measured (gel time, mechanical properties, size-exclusion chromatogram, volatiles content, resin flow), but a very slight decrease in epoxy content was observed. The property most affected was tack, which showed a definite decrease.

The findings discussed above will be considered later in the light of those observed in this work.

2. EXPERIMENTAL

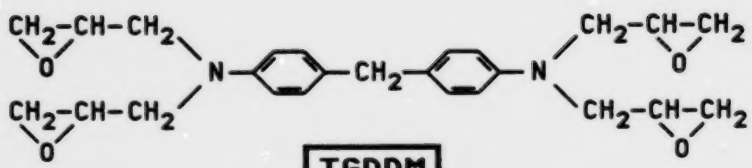
2.1 MATERIALS

The composite system chosen for intensive study was Rigidite 5208/WC3000-42", sold by Narmco Materials, Inc. (Anaheim, California). The reinforcement consists of Celion graphite fibres, 3000 fibres per yarn, woven in an 8-harness satin pattern (each warp yarn passing alternately over seven fill yarns and under one fill yarn). The woven fabric is impregnated with Narmco 5208 resin to a nominal resin content of 42% by weight and the prepreg is supplied on a plastic backing sheet in rolls 42 inches wide. The recommended cure schedule consists of a one-hour dwell at 275°F (135°C) followed by a two-hour cure at 350°F (177°C).

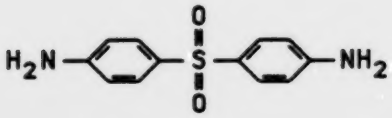
It has been reported [19-23] that Narmco 5208 consists primarily of three components. The major epoxy, which accounts for about 70% by weight, is based on TGDDM (tetraglycidyldiaminodiphenylmethane). A common commercial product of this type is Ciba-Geigy Araldite MY 720. The second most important component (about 22% by weight) is the curing agent DDS (diaminodiphenylsulphone); an example of a commercial grade of this material is Ciba-Geigy Hardener HT 976. There is also a minor epoxy (about 8% by weight) which is of the bisphenol A Novolac type (for example, Celanese Epi-Rez SU-8). The chemical structures of these are given in Figure 1. The DDS is a relatively pure material, but the epoxy resins consist of a mixture of monomer, oligomers, and other products (starting materials and by-products). A more detailed discussion of the Narmco 5208 system, including composition, analysis, and the nature of the curing reaction, is given in an earlier report [1].

The prepreg used in this study was obtained from Narmco Inc. by Canadair Ltd. It was Batch Number 1014, Roll Number 16, manufactured and tested on September 26, 1984. The following physical test data were provided by the manufacturer:

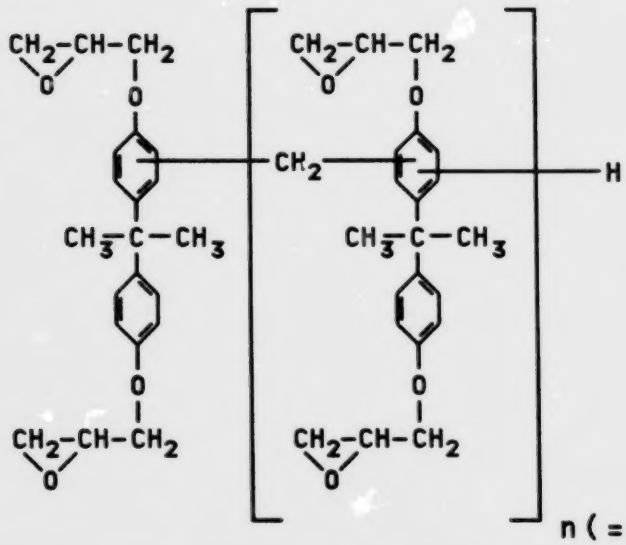
Property	First roll	Last roll	Overall
Resin solids:			42%
Fibre weight:			376 g/m^2
Volatiles content:	0.7%	1.4%	
Flow:	28%	26%	
Gel time:	27 min 16 s	25 min 8 s	



TGDDM



DDS



n (= 0, 1, 2, ...)

Bisphenol A Novolac Epoxy

Upon reception, the prepreg was stored in a freezer. On October 15, 1984, it was transferred to NRCC's Industrial Materials Research Institute where it was thawed, unrolled, and cut into twenty-three sheets approximately eight feet long. Of these, twenty were hung lengthwise in a rack in a controlled-atmosphere laboratory at ambient temperature and 50% relative humidity. Of the remaining three, one (the "control" sample) was immediately returned to Canadair Ltd. for physical testing and fabrication of mechanical test panels, one was stored in a freezer at -25°C at IMRI, and one was sealed in a plastic bag with "Drierite" desiccant and kept in the same laboratory as the suspended sheets. The plastic backing sheet was left in place, so that only one side of the prepreg was fully exposed. The sheets suspended in the rack were separated by about 4-5 inches.

At chosen intervals over a period of 66 days, one sheet of prepreg was removed from the rack. A strip one foot wide was cut for chemical analysis at IMRI and the remaining seven feet was transferred to Canadair Ltd. for physical testing and preparation of mechanical test panels. Both the chemical and physical testing were done on the day the sheet was removed from the rack. A "control" sample for chemical testing was taken from the "control" sheet returned to Canadair on the first day. The sheet stored under dry conditions was tested after 50 days, and the sheet stored in a freezer after 87 days.

2.2 EXPOSURE CONDITIONS

Temperature and relative humidity in the controlled-atmosphere laboratory were monitored frequently over the 66-day exposure period. The average values (based on 54 readings) were as follows:

Temperature:	21.5°C	(standard deviation 0.7°C)
Relative humidity:	49.2%	(standard deviation 2.4%)

2.3 TESTING PROCEDURES

The methods used are briefly described below. Physical and mechanical testing was done by Canadair according to its standard testing procedures; detailed methods are given in Canadair Materials and Process Specification CMS 532-05. In most cases these are similar to methods published by the American Society for Testing and Materials (Annual Book of ASTM Standards, Volume 15.03). Chemical testing was performed at IMRI based on the methods developed as described in earlier reports [2,3,4].

2.3.1 Physical Testing

2.3.1.1 Resin content

This was determined as part of the chemical testing procedures. For liquid chromatography [3], two separate prepreg specimens (about 5 x 5 cm) were solvent extracted in three stages with 50, 30, and 20 mL of tetrahydrofuran. After extraction, the fibre reinforcement was dried and weighed, and the weight of resin extracted was determined by subtraction from the initial prepreg weight. For infrared spectroscopy [2] one specimen was extracted using acetone as solvent. The resin content of the specimens used for DSC analysis was also determined, using a thermogravimetric method involving decomposition in an oxygen atmosphere [4].

2.3.1.2 Volatiles content

Details: CMS 532-05, Section 6.1.2, and ASTM D3530.

This was determined both at IMRI and at Canadair. A square of prepreg about 4 x 4 inches is weighed before and after heating at 350°F (177°C) for 20 minutes. The difference is taken to be the volatiles content. The IMRI values are the average of two specimens, the Canadair values the average of three.

2.3.1.3 Resin flow

Details: CMS 532-05, Section 6.1.3, and ASTM D3531.

Two plies of prepreg of size 3 x 3 inches are weighed, sandwiched together between porous Teflon cloth and glass cloth bleeder, and pressed at 85 psi (586 kPa) for 1 minute in a press preheated to 350°F (177°C). After a 10-minute cure, the specimen is removed and cooled. The weight of the resin squeezed out is determined and expressed as a percentage of the total prepreg weight. Reported values are the average over three specimens.

2.3.1.4 Gel time

Details: CMS 523-05, Section 6.1.4, and ASTM D3532.

Several plies of prepreg are stacked between two sheets of nonporous material and pressed between platens heated to 350°F (177°C). The resin squeezed out is manipulated

with a probe at this temperature. The time at which the resin passes from a "stringy" state to a rubbery state is taken as the gel time. Reported values are the average of three determinations.

2.3.2 Mechanical Testing

Test panels are made by vacuum-bag autoclave curing in a two-stage process. In the first stage, the prepreg is subjected to vacuum and an external pressure of 10 psi (69 kPa) while it is heated to 275°F (135°C) and kept there for 1 hour. At this point, the pressure is increased to 85 psi (586 kPa), the bag is vented to atmosphere, the temperature is increased to 350°F (177°C), and the cure is completed by maintaining this temperature for 2 hours.

2.3.2.1 Tensile properties

Details: CMS 532-05, Section 6.3.2, and ASTM D3039.

A test panel is made from 4 plies of prepreg, giving a final thickness of about 0.055 in. (1.4 mm). Suitable tensile specimens (10 in. x 0.5 in.) are cut from the laminate and strained to rupture at a crosshead speed of 0.050 inches per minute. At least five specimens are tested. The following properties are evaluated: ultimate tensile stress, ultimate tensile strain, tensile modulus of elasticity.

2.3.2.2 Compressive properties

Details: CMS 532-05, Section 6.3.3, and ASTM D695.

A test panel is made from 6 plies of prepreg, giving a final thickness about 0.083 in. (2.1 mm). At least five specimens of the specified geometry are prepared and subjected to compression at 0.050 inches per minute until they rupture. The following properties are evaluated: ultimate compressive stress, ultimate compressive strain, compressive modulus of elasticity.

2.3.2.3 Short-beam shear strength

Details: CMS 532-05, Section 6.3.4, and ASTM D2344.

A test panel is made from 6 plies of prepreg (final thickness about 0.083 in. or 2.1

mm). At least five specimens of the required geometry (0.58 in. x 0.25 in.) are prepared and subjected to shear stress at a load rate of 0.05 inches per minute until breakage occurs. The apparent shear strength is calculated.

2.3.3 Chemical Testing

2.3.3.1 Infrared spectroscopy — transmission

Details: Reference 2.

A specimen of prepreg is extracted with acetone and a thin film of resin is carefully cast on a potassium bromide disk. The transmission spectrum is measured, converted to absorbance, and used to calculate "epoxy" and "sulphone" indices which are a measure of the unreacted epoxy content and the total hardener content respectively. Further details are given in Section 4, "Infrared Spectroscopy". The instrumentation used for this work was a Nicolet Instruments Model 170SX Fourier transform infrared spectrometer equipped with a wide-range liquid-nitrogen-cooled mercury cadmium telluride detector. Spectra were recorded using an accumulation of 128 scans with a resolution of 4 cm^{-1} and Happ-Genzel apodization. Each calculated index corresponds to the average over three to five specimens prepared from a single acetone extract.

2.3.3.2 Infrared spectroscopy — attenuated total reflection

Details: Reference 2.

With this method, solvent extraction of the prepreg is not required. Instead, the prepreg surface is measured directly by pressing it against a germanium prism through which the infrared beam passes. This method is not only easier and faster than the transmission method, but it also avoids the problem of preparing a film of uniform thickness. Spectra were recorded under the same conditions as in transmission using a reflection accessory from Harrick Scientific Corp. This was a Twin Parallel Mirror Reflection Attachment (Variable Angle Manual) with Internal Reflection Accessory and single-pass parallelogram prism (KRS-5 or germanium, 45°, 50 x 10 x 3 mm). Epoxy and sulphone indices were calculated in the same way as in transmission. Each reported index corresponds to the average of five different specimens taken from the same sample of prepreg.

2.3.3.3 Infrared spectroscopy — diffuse reflection

Details: Reference 2.

This method also allows direct measurement of the spectrum of the prepreg surface and does not require intimate contact with the sample. Although excellent for qualitative work, it has been found to be of limited value for quantitative work. Diffuse reflection spectra were recorded under the same conditions as in transmission using a "praying mantis" accessory from Harrick Scientific Corporation. Powdered compacted potassium bromide was used as reference material.

2.3.3.4 Reverse-phase liquid chromatography

Details: Reference 3.

A specimen of prepreg (about 5 x 5 cm) is solvent-extracted with tetrahydrofuran, a known quantity of acetophenone internal standard is added, and the solution is injected onto a reverse-phase column where it is separated into its individual components. The column used is packed with a nonpolar octadecyl bonded phase (MCH-5-n-CAP from Varian, 30 cm long x 4 mm i.d., 5 μm particles). Gradient elution is used with acetonitrile-water as eluent (50:50 to 100% ACN in 15 minutes). The different components are detected at the end of the column with a UV detector set at 230 nm. The main peaks in the resulting chromatogram are measured in terms of area or height and "normalized" with respect to the acetophenone internal standard. The values obtained are a measure of the amount of the particular component in the resin.

2.3.3.5 High-speed reverse-phase liquid chromatography

Details: Reference 3.

This is similar to the previous case except that the separation is achieved using a column packed with 3 μm particles (Ultra-fast C_{18}-3 from Varian, 4 cm long x 4.6 mm i.d.). Gradient elution is done with acetonitrile-water, but the composition changes linearly from 20:80 ACN-H_2O to 100% ACN in 3 minutes. With the high-speed column the overall analysis time is much faster, although the resolution is not quite as good as with the "standard" column. The data treatment is similar to the previous case.

2.3.3.6 High-performance size-exclusion chromatography

Details: Reference 3.

The same solutions used for reverse-phase HPLC were also analysed by SEC using a PLgel column, 30 cm long x 7.5 mm i.d., packed with 5 µm particles of a poly(styrene/divinylbenzene) copolymer. In this case, the separation is achieved on the basis of molecular size, so the chromatogram is quite different from the reverse-phase chromatogram. The eluent consists of 100% tetrahydrofuran at a flow rate of 1.0 mL/min, and the components are detected using a refractive index detector. The peaks in the chromatogram are measured quantitatively in terms of their relative area, expressed as a percentage of the total area of the chromatogram. An index is also obtained by dividing the total area of the peaks corresponding to molecules of higher molecular weight by the area of the peaks which correspond mainly to monomers. This index has been used as an indicator of the degree of polymerization of the resin.

2.3.3.7 Pyrolysis - capillary gas chromatography

Details: Reference 4.

Analyses were done using a pulse-mode pyrolyzer (Chemical Data Systems Model 170) coupled to a Model 6000 Varian gas chromatograph. A sample of prepreg (about 1 mg) is put in the centre of an open quartz tube about 20 mm long which is then placed inside a platinum coil probe. The sample is pyrolyzed at 650°C for 10 seconds, and the degradation products are injected onto a capillary gas chromatographic column (DB-17, 30 m x 0.259 mm). The temperature program is as follows: 50°C to 60°C at 2°C/min, then 60°C to 250°C at 10°C/min. The components are detected using a flame ionization detector. The ratios of the areas of certain selected peaks in the chromatogram against that of the peak of aniline are used to characterize the sample.

2.3.3.8 Differential scanning calorimetry

Details: Reference 4.

DSC analyses were done using a SETARAM Model CDP111 apparatus. A prepreg sample weighing about 40 mg (about 3 x 15 mm in size) is put in a platinum crucible and a DSC curve is recorded at a heating rate of 5°C/min with nitrogen as the atmosphere. Only one peak is observed, and the enthalpy of curing ΔH is determined by measuring the area under the curve between 130°C and 273°C. This value must be divided by the exact mass

of epoxy resin in the sample in order to obtain reproducible values. This mass is determined by doing a thermogravimetric analysis on the same sample.

2.3.3.9 Thermogravimetric analysis

Details: Reference 4.

Thermogravimetric analyses were done on a SETARAM Model B70 thermobalance at 10°C/min under an oxygen atmosphere. The mass is obtained from the inflexion point corresponding to the end of oxidation of the resin and the beginning of oxidation of the graphite fibres (about 565°C).

2.4 SAMPLE DESIGNATION

Throughout the remainder of the report, the samples exposed to room temperature and 50% relative humidity are designated by a number corresponding to the number of days of exposure. The others are labelled "Control" (unexposed sample), "50D" (50 days exposure, ambient temperature, dry conditions), and "87F" (87 days storage in freezer). For some of the tests (for example, HPLC) two different specimens were analysed separately and the results are reported for both; these are labelled "A" and "B" to distinguish them.

3. PHYSICAL AND MECHANICAL TESTING

3.1 PHYSICAL TESTING

The quantitative data from the physical testing are all given in Table 1.

3.1.1 General Appearance

After three weeks exposure, the prepreg had lost most of its "tack" and separated quite easily from the plastic backing sheet. Although harder than at the beginning, it was still quite pliable. By six weeks, it had become fairly rigid. The sample exposed for 50 days under dry conditions was also hard and non-tacky. The sample stored in a freezer for 87 days remained tacky and pliable.

3.1.2 Resin Content

The variation of the resin content, as determined by solvent extraction or thermogravimetric analysis, is illustrated graphically in Figure 2. The THF results come from the liquid chromatography experiments, where two separate extractions were done. All the samples gave clear THF solutions. The acetone results are from infrared spectroscopy work and are based on one extraction only. With acetone, the samples exposed longer than 30 days gave cloudy solutions, indicating that the resin had polymerized to the point where the higher-molecular-weight components have limited solubility in acetone. Consequently, the acetone results for exposure times longer than 30 days are less reliable. They are enclosed in parentheses in Table 1 and are not included in Figure 2. The TGA results were obtained for a limited number of samples, and the number of specimens analysed in for each sample varied.

The scattering in Figure 2 is attributed to sampling rather than to errors in determining the percent weight extracted. The relatively small specimens used (about 5 x 5 cm for solvent extraction, smaller for thermal analysis) do not always contain the same amount of resin as the batch as a whole because of variations in resin distribution within the graphite cloth. The average resin content, based on all the points shown in Figure 2, is 42.9% with a standard deviation of 1.8%.

Table 1. Physical testing results.

Sample	% Resin extracted (THF)	% Resin extracted (acetone)	% Resin by TGA	Volatiles content (%) (IMRI)	Volatiles content (%) (Canadair)	Resin flow (%)	Gel time (min)
Control	42.5, 43.6	44.7	40.0, 44.0, 44.6	1.8	1.9	26.2	21.0
2	43.8, 45.2	43.8		1.4	1.3	26.0	19.0
4	42.9, 43.9	45.4		1.2	1.3	26.1	19.0
7	42.7, 46.0	45.2	41.5, 43.6	1.1	1.1	23.1	20.0
9	42.4, 43.1	41.1		0.9	1.2	26.0	20.0
11	41.8, 43.2	43.2		1.0	1.3	25.6	18.0
14	40.5, 45.8	44.4		0.9	1.0	26.4	19.7
17	42.5, 43.5	43.5	39.2, 39.2, 39.3, 40.3	0.9	1.1	27.7	19.0
21	41.4, 42.8	41.1		0.8	0.9	25.3	18.0
25	42.0, 43.5	42.1		0.7	1.0	26.8	16.4
29	43.0, 43.6	43.7		0.9	1.0	25.9	15.6
32	43.2, 44.5	(41.2)	38.6, 45.0	0.9	1.0	26.5	16.0
35	41.1, 44.6	(41.8)		1.0	0.9	26.1	15.3
38	40.6, 40.9	(41.7)		0.8	0.9	26.3	13.3
42	42.1, 42.8	(40.1)	42.4, 45.1	0.8	0.7	23.1	12.8
45	39.8, 42.8	(40.5)		0.9	0.9	26.9	9.9
52	42.4, 42.7	(37.2)		0.8	0.8	25.5	11.1
59	40.3, 42.9	(36.7)	46.1, 46.6	0.7	0.8	21.8	7.7
66	43.5, 44.4	(36.2)	43.9, 45.0, 45.5	0.7	0.9	24.6	7.2
50D	42.7, 42.9	(39.9)		0.9			
87F	41.4, 44.1	42.0	41.3, 44.1	1.4	1.4	26.5	20.9

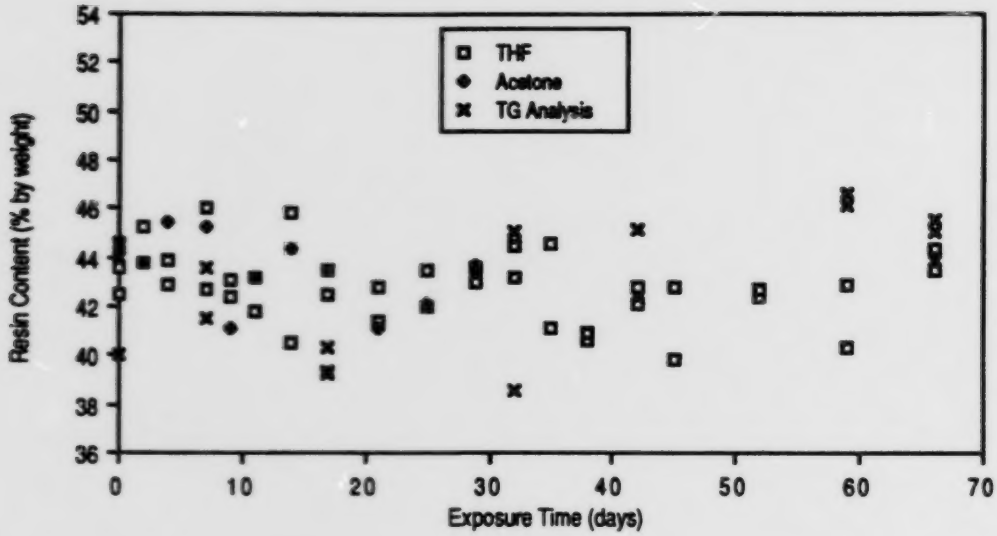


Figure 2. Variation of the measured resin content (as determined by THF extraction, acetone extraction, and thermogravimetric analysis) as a function of prepreg exposure time.

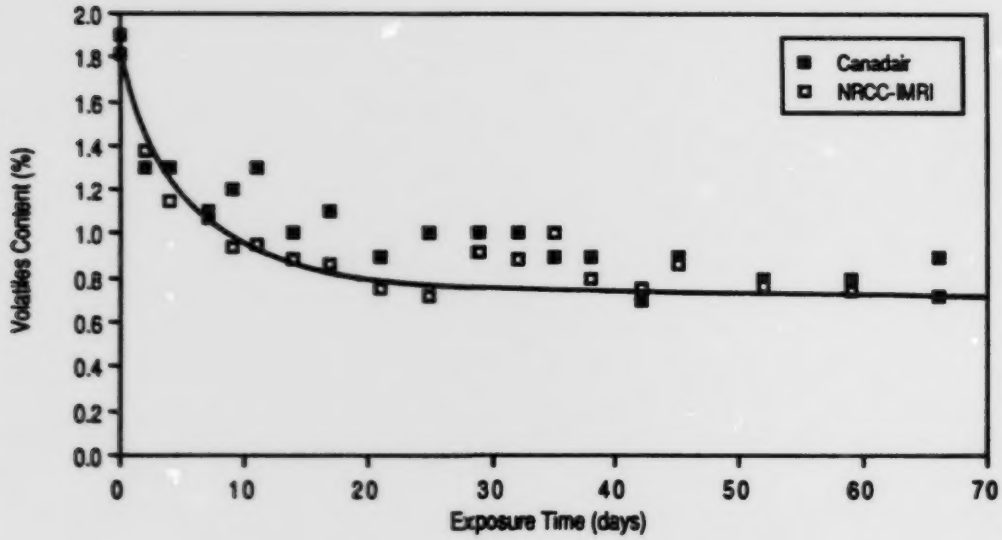


Figure 3. Variation of the volatiles content as a function of the prepreg exposure time.

3.1.3 Volatiles Content

The results obtained both at Canadair and at IMRI are shown in Figure 3. The two sets are in good agreement. Both show an initial volatiles content of about 1.9% which drops rapidly during the first few days exposure, then more gradually, levelling off at about 0.8% after 20 days or so.

The nature of the volatile materials was investigated using FTIR spectroscopy. Figure 4 shows the diffuse reflectance infrared spectra of three different samples of prepreg: (a) an unexposed sample; (b) a sample exposed to ambient temperature and 50% R.H. for 29 days; (c) a specimen of the unexposed sample after heating at 177°C for 5 minutes. The unexposed sample shows a distinct peak near 1710 cm^{-1} which is absent from the other two spectra. Attenuated total reflectance spectra of fresh prepreg show the same peak. Sometimes a peak also appears in the same region in transmission spectra, but in this case it is attributed to residual acetone from the extraction procedure; it disappears when the specimen is placed under vacuum for a longer time to remove the solvent completely. However, no acetone is used in the sample preparation for reflection spectra, so in these cases the peak must be due to a volatile component of the prepreg formulation.

In order to identify this component, a sample of fresh prepreg was placed in the bottom of a 10 cm long gas cell. The IR transmission spectrum was measured both before and after the cell was heated at 177°C for 5 minutes. Both spectra showed some peaks due to water vapour and carbon dioxide; when these were removed by spectral subtraction, the spectra shown in Figure 5a and 5b were obtained. They are the same except for the intensity. A search of a library of vapour phase spectra showed the volatile component to be acetone, Figure 5c. The spectra match very well and there is no evidence of other components. For example, methyl ethyl ketone, which is sometimes found in prepregs, has a spectrum sufficiently different from acetone so that it can be concluded that there is very little or none present in this case. The volatile component of Narmco 5208 prepreg, therefore, consists almost entirely of moisture and acetone.

3.1.4 Resin Flow

The results are plotted in Figure 6. Within the limitations of the experimental error involved, which is indicated by the scatter, there appears to be no significant change with aging. The average value based on the results given in Table 1 is 25.6 minutes, with a standard deviation of 1.4 minutes.

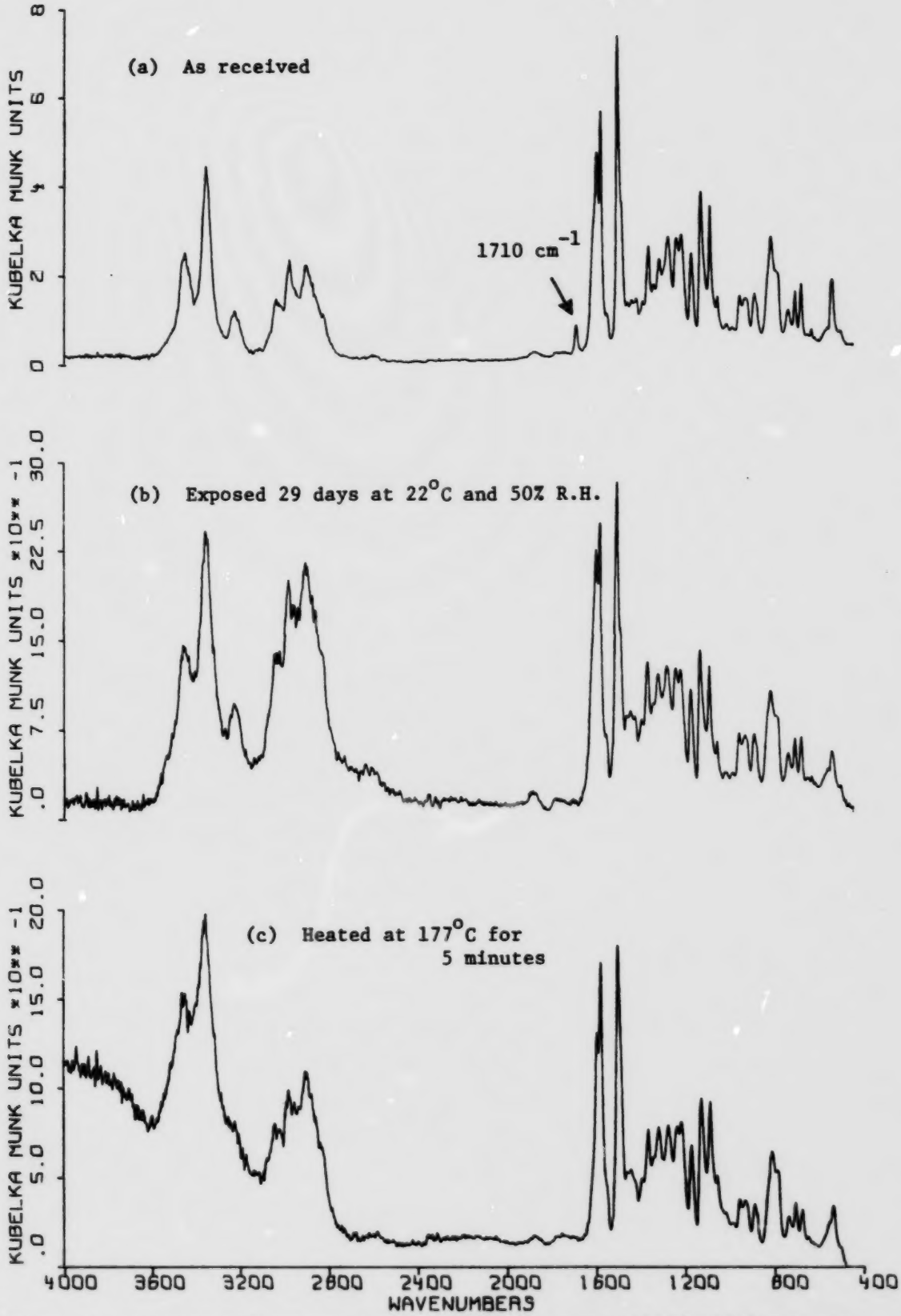


Figure 4. Diffuse reflectance FTIR spectra of Narmco 5208/WC3000 prepreg.

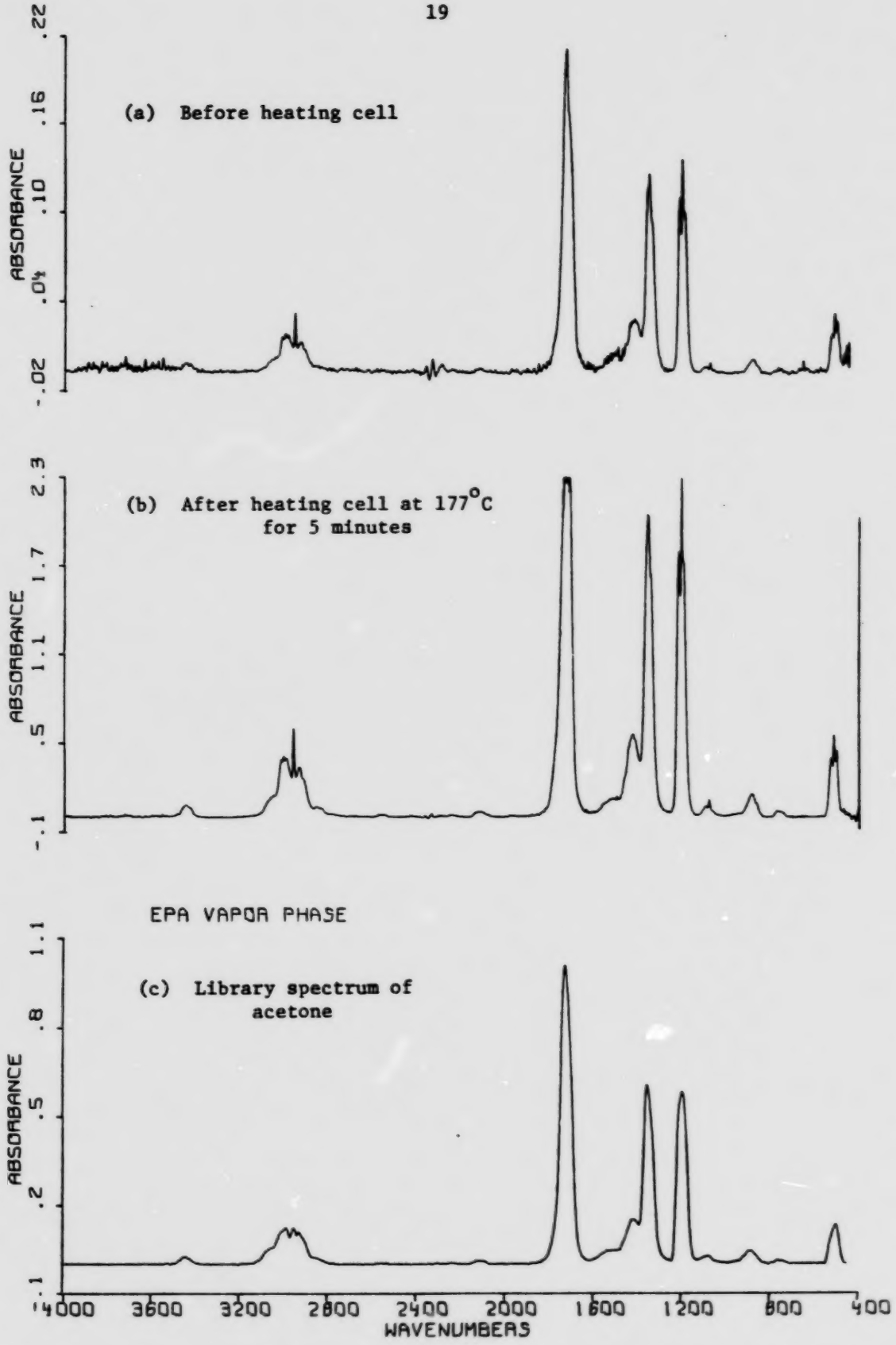


Figure 5. FTIR transmission spectra of volatile component of Narmco prepreg.

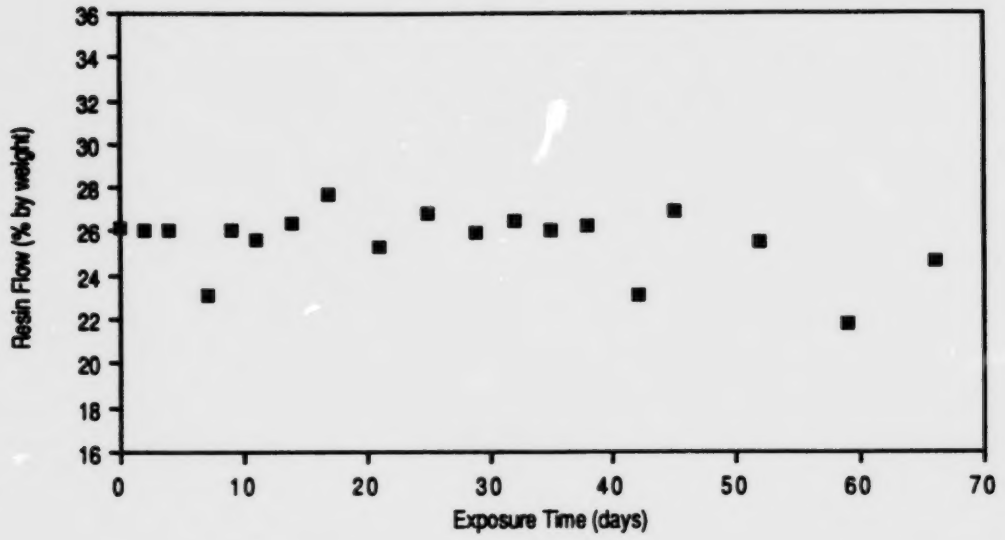


Figure 6. Variation of resin flow as a function of prepreg exposure time.

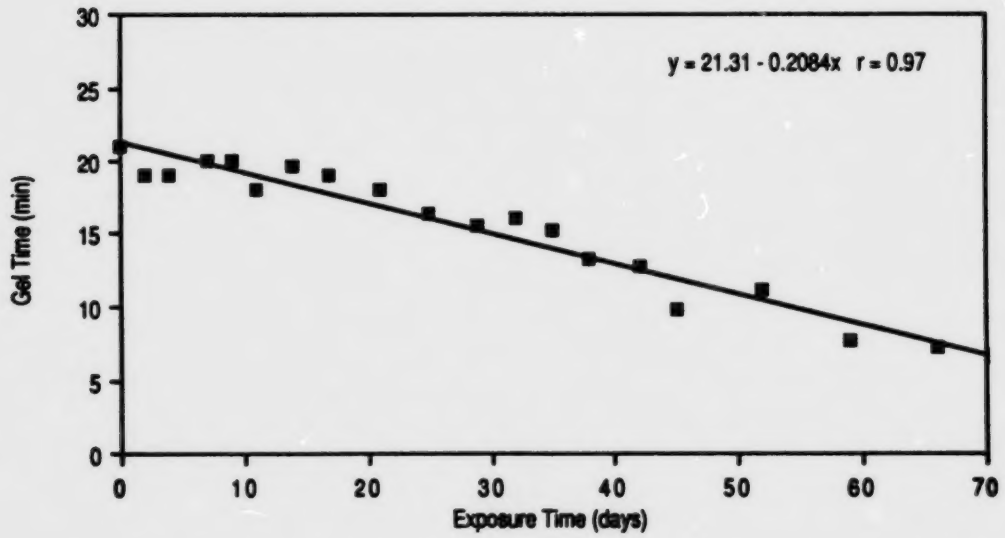


Figure 7. Variation of gel time as a function of prepreg exposure time.

3.1.5 Gel Time

The data are plotted in Figure 7. In this case there is an obvious decrease with time. A linear least squares fit gives a correlation coefficient of 0.97 and the following equation:

$$\text{Gel time (min)} = 21.3 - 0.208 \times (\text{number of days exposure}).$$

Of the physical properties measured, the gel time is by far the most sensitive to the prepreg aging.

3.1.6 Tack

Although no quantitative test was done to evaluate this property, it was obvious that the first observable physical change on aging was a fairly rapid loss of tack. This appears to be directly related to a drop in the volatiles content, which is due to evaporation of acetone from the prepreg. Larsson and Wirsén [18] have observed a similar correlation between tack and volatiles content. Hinrichs and Thuen [7] have reported that the volatiles content of Narmco 5208 is almost exclusively (>97%) water of atmospheric origin. However, the prepreg used in their work was probably solvent-free unidirectional tape, manufactured using a hot-melt impregnation process. The prepreg used in this work was based on woven fabric, which apparently is impregnated using a solvent coating process.

An experiment was performed to determine the effect of the acetone on prepreg tack. A fresh sample of prepreg was cut in two and half was placed under vacuum for 24 hours without heating. Both halves were checked for volatiles content and chemical composition (reverse-phase liquid chromatography), with the following results:

Property	Fresh prepreg	Vacuum-treated prepreg
Volatiles content (%)	1.40	0.82
RPLC: DDS peak	3.97	3.99
RPLC: TGDDM peak	12.86	13.07
RPLC: DGEBA peak	1.75	1.82
RPLC: Reaction product peak	1.68	1.69

The RPLC results show that no significant resin advancement occurred during the vacuum treatment. However, the volatiles content decreased substantially, due to loss of acetone. This was accompanied by a definite change in tack. When two surfaces of fresh prepreg

were placed in contact and then pulled apart, "strings" of resin formed between the two. When this was done with the vacuum-treated prepreg, this did not occur.

It appears then that the tack properties of Narmco 5208 prepreg are closely related to the volatiles content, and in particular, to the presence of acetone. When the prepreg is exposed to the atmosphere, the rapid drop in volatiles content which occurs in the first few days is related to loss of acetone and is accompanied by a loss of tack. After a couple of weeks the prepreg equilibrates with the atmosphere and the volatiles content stabilizes around 0.8%, most of which, if not all, can be attributed to moisture. This is the same saturation level reported for moisture in Narmco 5208 by Hinrichs and Thuen [7].

3.1.7 Discussion

It is obvious from the above results that exposure of the prepreg to ambient temperature and humidity causes significant changes in the resin properties.

Apart from tack, the physical property most affected by the aging is the gel time, which drops from 21 minutes to 7 minutes over the 66-day exposure period. This is a drastic change and would certainly be expected to affect the prepreg processing. With a short gel time, the system would crosslink in the mould before the prepreg layers could be properly consolidated and excess resin squeezed out.

It might be thought that since the gel time is fairly sensitive to the prepreg aging, it could be sufficient for checking the extent of aging, and that physicochemical methods are not really necessary. However, there are two reasons why this is not so. Firstly, the gel time determination, as described in Section 2.3.1.4, is a rather subjective test. It may be reliable when done in a given laboratory by a given technician, as in the present case, but when performed in different laboratories the results may not be consistent. This could be overcome by determining the gel time instrumentally, but this requires sophisticated rheological equipment. Secondly, the gel time is only a single parameter, and therefore gives limited information. Although it is sensitive to the resin advancement, it is also affected by variations in the initial composition of the resin [24]. It is possible, for example, that a batch could have a low hardener content but a high degree of advancement. In such a case, the two would compensate and the gel time would appear normal, even though the batch would not be acceptable. Physicochemical test methods could detect the problem.

In view of the changes observed for the gel time, one might expect that the resin flow would be affected also, but this is not the case. However, the flow test is done under "ideal" laboratory conditions using a small sample in a simple press. Martin and Tungare [25] have done a study of the flow test under similar conditions, and found that the flow is

complete in under six minutes. Since the gel time is longer than this, even for the highly aged samples, it is not surprising that the flow is hardly affected. This would not be true, however, in the case of a real part, where the flow behaviour is usually much more complex. In such a case, there is a much greater chance that the system will gel before the flow is complete, if the batch is significantly aged. The flow test must therefore be considered inadequate as an indicator of prepreg aging.

3.2 MECHANICAL TESTING

The results of the mechanical testing are summarized in Table 2. Because of the substantial amount of work involved, fewer samples were tested than in the case of physical and chemical testing. A total of eleven samples were tested (approximately one per week).

Table 2. Mechanical testing results.

Sample	Tensile strength (ksi)	Tensile modulus (Msi)	Ultimate strain (μin/in)	Compressive strength (ksi)	Compressive modulus (Msi)	Short beam shear (ksi)
Control	92	9.0	10640	110	9.8	11.1
7	103	10.7	10110	95	12.1	8.5
14	112	10.6	10880	106	10.7	10.7
21	105	9.9	11120	91	9.8	7.5
29	79	9.3	8960	83	11.1	7.0
35	91	9.2	10280	91	9.9	7.2
42	108	9.6	11340	87	9.8	6.9
52	107	10.0	11000	104	10.4	9.0
59	106	9.7	11010	88	8.9	7.6
66	93	9.7	9650	80	9.5	7.7
87F	100	10.2	9920	83	9.6	6.9

3.2.1 Tensile Strength

The variation is shown graphically in Figure 8. As is common in mechanical testing, a fair degree of scatter is observed. There appears to be no significant dependence on the prepreg exposure time.

3.2.2 Tensile Modulus

The behaviour is shown in Figure 9. As in the case of the tensile strength, no significant correlation was observed.

3.2.3 Ultimate Tensile Strain

Again, as shown in Figure 10, no correlation was found.

3.2.4 Short Beam Shear Strength

The data are shown graphically in Figure 11. In spite of the scatter, there is some evidence of a slight downward trend with respect to the time of prepreg exposure.

3.2.5 Compressive Strength

The behaviour is shown in Figure 12. The situation is similar to the previous one, with a slight downward trend.

3.2.6 Compressive Modulus

Figure 13 shows the results. Once more, there is a downward trend.

3.2.7 Discussion

Previous studies of epoxy systems involving the effect of variations in chemical composition on mechanical properties [24, 26-29] have generally shown no significant correlation unless the variations were drastic. This may be because of the large degree of scatter often associated with mechanical test results, as in the present work, which makes it

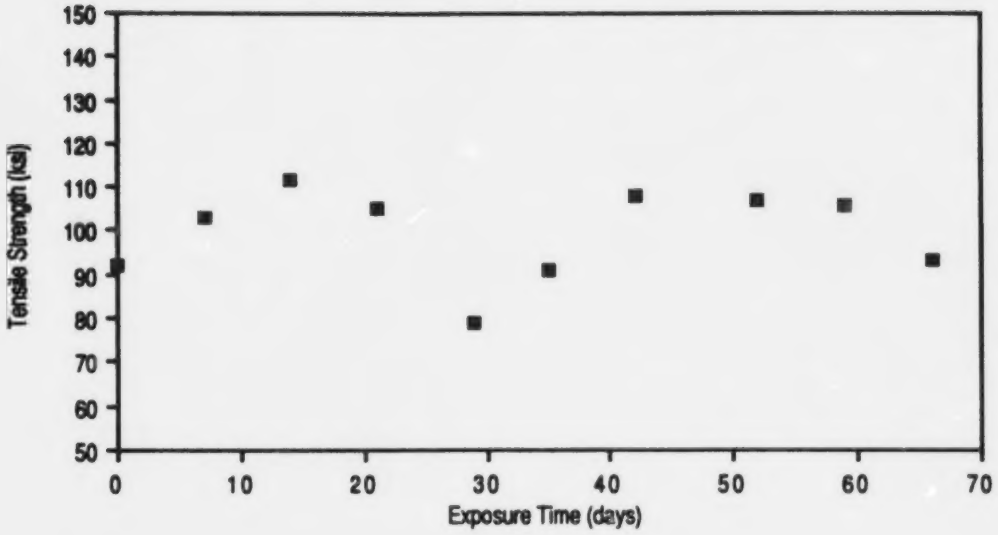


Figure 8. Variation of tensile strength as a function of prepreg exposure time.

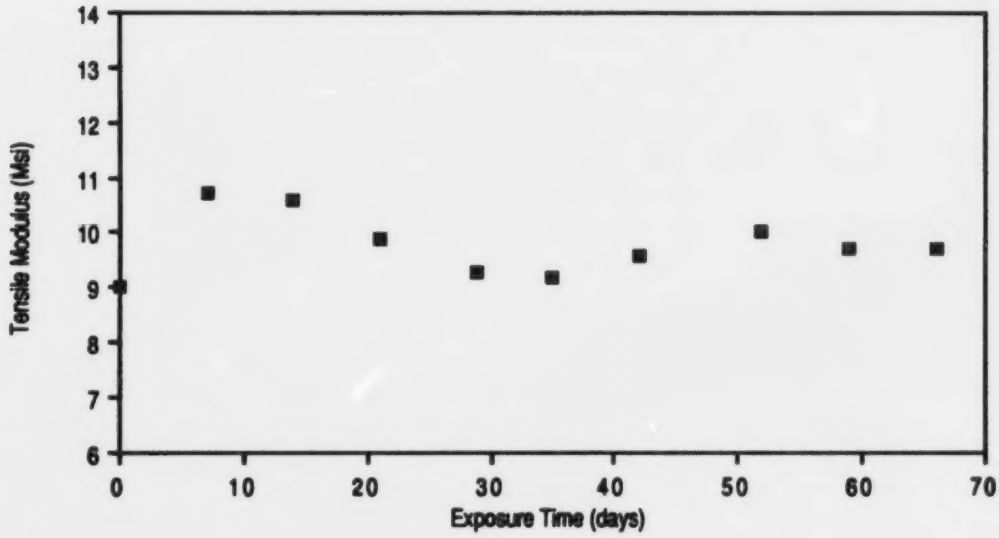


Figure 9. Variation of tensile modulus as a function of prepreg exposure time.

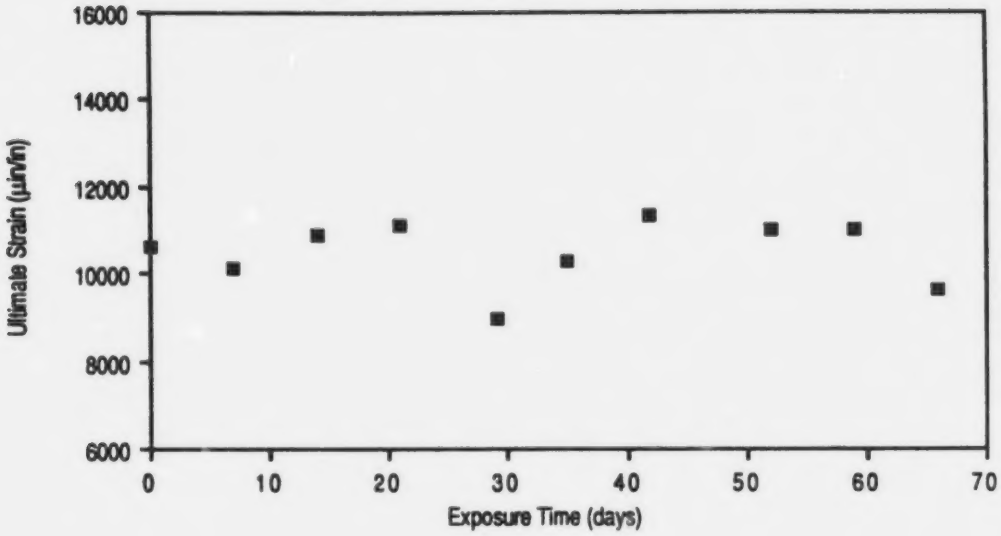


Figure 10. Variation of ultimate tensile strain as a function of prepreg exposure time.

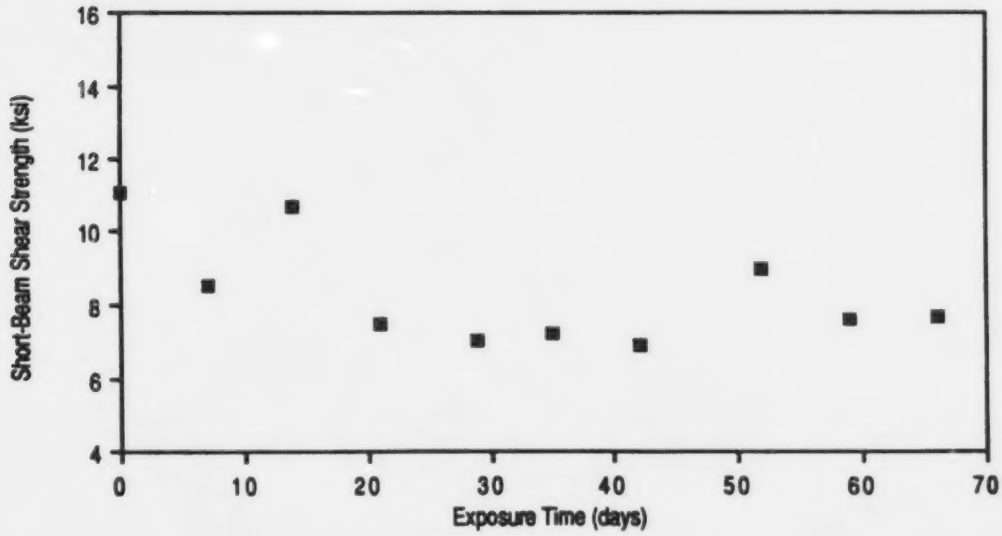


Figure 11. Variation of short beam shear strength as a function of prepreg exposure time.

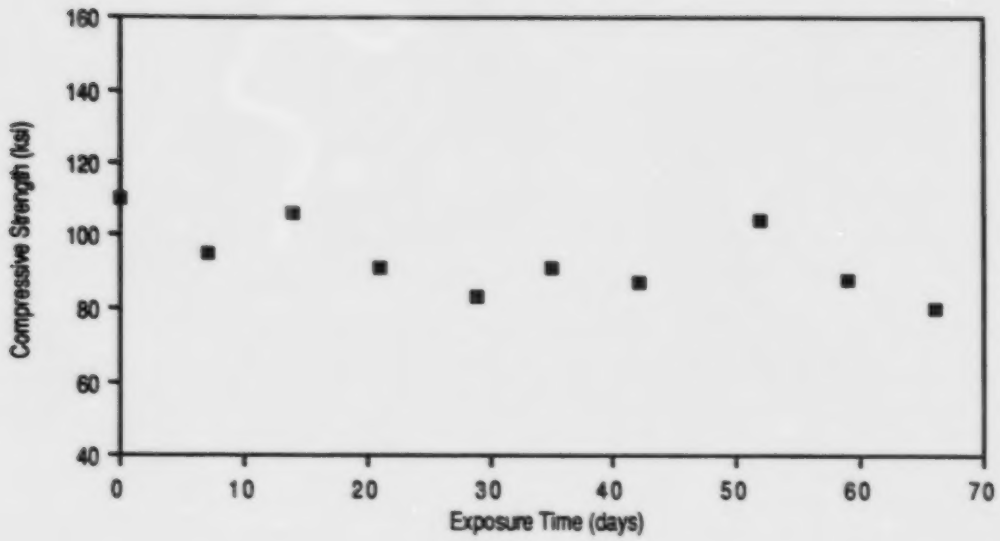


Figure 12. Variation of compressive strength as a function of prepreg exposure time.

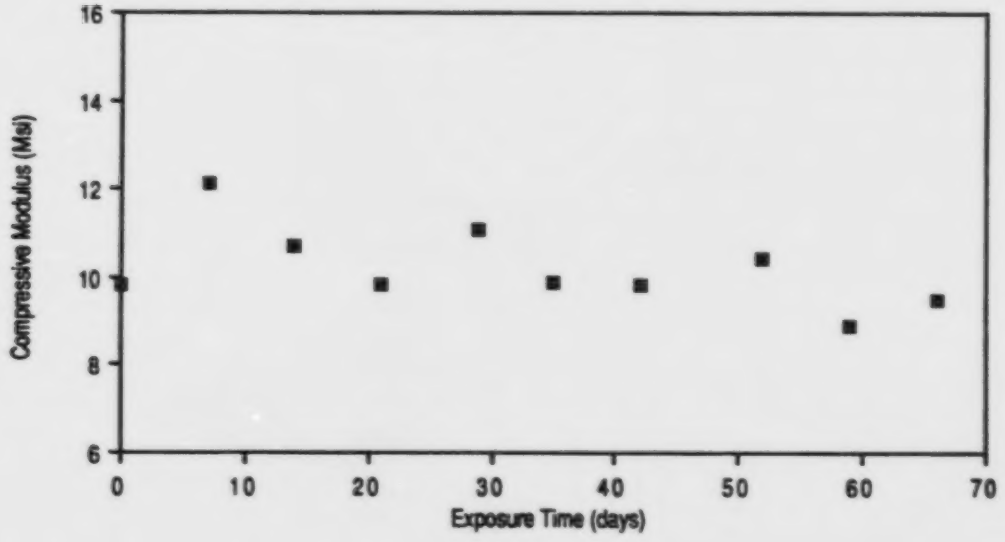


Figure 13. Variation of compressive modulus as a function of prepreg exposure time.

difficult to discern any correlations which may exist. Because of the slight downward trend which appears to exist in some of the figures just discussed, a more quantitative treatment of the data was attempted by applying simple linear regression analysis. The results are summarized in Table 3. The error limits specified for the slopes and intercepts are the standard deviations calculated according to the usual methods [30]. They correspond to a confidence level of greater than 97%.

Table 3. Linear regression results for mechanical properties.

Property	Intercept	Slope	Correlation coefficient
Tensile Strength	98.9 ± 6.3	0.02 ± 0.16	0.044
Tensile Modulus	9.89 ± 0.34	-0.0037 ± 0.0087	-0.148
Ultimate Tensile Strain	10510 ± 460	0 ± 12	-0.008
Short Beam Shear Strength	9.53 ± 0.77	-0.037 ± 0.020	-0.553
Compressive Strength	102.2 ± 5.0	-0.27 ± 0.13	-0.591
Compressive Modulus	10.94 ± 0.46	-0.023 ± 0.012	-0.556

In view of the limited amount of data available, it is perhaps immoderate to attach too much significance to the statistical calculations performed, but it is tempting to make conjectures. It is very interesting to note that the three tensile properties show no significant dependence on prepreg aging, whereas the compressive properties and short beam shear strength all show evidence of a slight decrease with time (correlation coefficients around -0.5 to -0.6). This is exactly the behaviour which might be expected on the basis that tensile properties are determined mainly by the fibre reinforcement, whereas compressive and interlaminar shear properties are more closely associated with the organic matrix. Thus the latter would be expected to be more affected by changes in resin chemistry, which is exactly what is observed.

The changes observed for the short beam shear and the compressive properties are not particularly large, being of the order of -0.2% to -0.4% per day of prepreg exposure. However, it must be remembered that these results were obtained for ideal specimens -- simple flat panels made under laboratory conditions. For complex parts made in a factory environment, the effects could be much more important. Furthermore, the long-term behaviour could be affected to a greater extent than the short-term properties, which are free

of the effects of environmental exposure.

These results, then, provide evidence that changes in chemical composition resulting from prepreg aging can have a significant effect on the mechanical behaviour of parts made from the prepreg. This underlines the importance of having reliable physicochemical test methods for checking the prepreg.

4. INFRARED SPECTROSCOPY

4.1 TRANSMISSION

A typical Narmco 5208 transmission spectrum is shown in Figure 14. The peaks used for quantitative analysis are the aromatic ring band at 1517 cm^{-1}, the epoxy ring bands at 973, 952, and 906 cm^{-1}, and the DDS (sulphone) bands at 1146, 1105, and 1073 cm^{-1}. Peak areas are calculated with respect to baselines drawn between the valleys on either side, as shown in the figure. Dividing the epoxy band area by the aromatic ring band area gives an "epoxy index" which is a measure of the number of unreacted epoxy groups in the resin and is thus related to the degree of aging. Similarly, taking the ratio of the sulphone band against the aromatic band gives a "sulphone index" which is a measure of the total amount of DDS hardener in the system. Since the sulphone groups are not destroyed in the curing reaction, this index should not be significantly affected by aging. For both epoxy and sulphone a "single" or a "multiple" index can be calculated depending on whether one or several peaks are used in the calculation. Thus the "single epoxy" index is based on only the peak at 906 cm^{-1}, whereas the "multiple epoxy" index is based on all three. Similarly, the "single sulphone" index is based on the peak at 1146 cm^{-1}, while the "multiple sulphone" index involves all three.

The calculated indices are listed in Table 4 and shown graphically in Figures 15 to 18. In these and in subsequent graphs, the error bars correspond to the calculated standard deviations.

The epoxy indices show a definite decrease with aging time. The variation appears to be linear up to about 50 days, beyond which point some deviation occurs. This may be due to a slowing of the epoxy reaction, but more likely it is related to the fact that the more highly aged samples were not completely soluble in acetone, as discussed in Section 3.1.2. Linear regression for the points corresponding to less than 50 days gives the following equations:

$$\text{Multiple epoxy index} = 0.407 - 0.00137 \times (\text{number of days exposure})$$

$$\text{Single epoxy index} = 0.135 - 0.000459 \times (\text{number of days exposure}).$$

In both cases, the rate of decrease based on the initial free epoxy content corresponds to 0.34% per day. Thus over a period of 50 days the number of unreacted epoxy groups drops by 17%. This is a quite significant change, so it is not surprising that the physical and even the mechanical properties are affected.

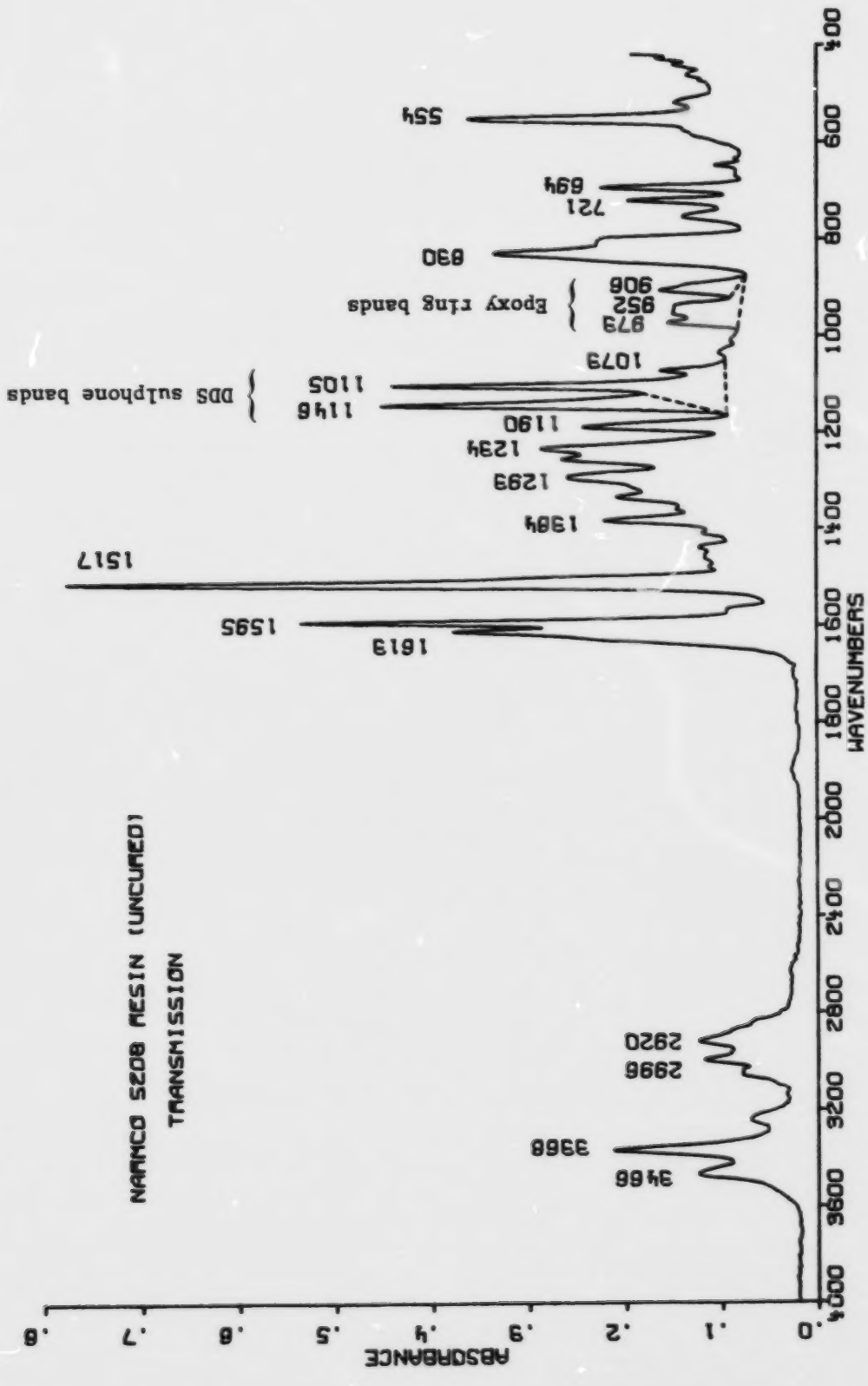


Figure 14. FTIR transmission spectrum of Narmco 5208 resin.

Table 4. Infrared spectroscopy results (transmission).

Sample	Single epoxy index		Multiple epoxy index		Single sulphone index		Multiple sulphone index	
	Value	SD	Value	SD	Value	SD	Value	SD
Control	0.136	0.001	0.409	0.002	0.439	0.001	1.055	0.004
2	0.135	0.001	0.405	0.003	0.436	0.004	1.053	0.012
4	0.133	0.001	0.400	0.004	0.430	0.004	1.045	0.003
7	0.132	0.001	0.397	0.004	0.427	0.003	1.038	0.019
9	0.130	0.001	0.391	0.001	0.435	0.002	1.061	0.008
11	0.131	0.001	0.393	0.004	0.436	0.001	1.066	0.002
14	0.129	0.001	0.387	0.003	0.432	0.002	1.070	0.007
17	0.128	0.002	0.388	0.006	0.431	0.001	1.063	0.005
21	0.125	0.001	0.376	0.001	0.426	0.001	1.064	0.005
25	0.125	0.002	0.376	0.006	0.423	0.003	1.074	0.008
29	0.121	0.001	0.365	0.003	0.417	0.003	1.059	0.010
32	0.120	0.001	0.359	0.002	0.415	0.002	1.075	0.009
35	0.118	0.001	0.355	0.003	0.411	0.004	1.069	0.001
38	0.120	0.001	0.357	0.002	0.411	0.005	1.075	0.018
42	0.117	0.001	0.354	0.003	0.404	0.004	1.057	0.009
45	0.114	0.001	0.345	0.002	0.404	0.004	1.066	0.013
52	0.112	0.002	0.341	0.004	0.389	0.002	1.060	0.010
59	0.112	0.001	0.338	0.002	0.388	0.001	1.073	0.001
66	0.111	0.002	0.332	0.005	0.379	0.003	1.076	0.009
50D	0.118	0.001	0.352	0.001	0.409	0.001	1.087	0.004
87F	0.133	0.002	0.398	0.005	0.430	0.003	1.039	0.015

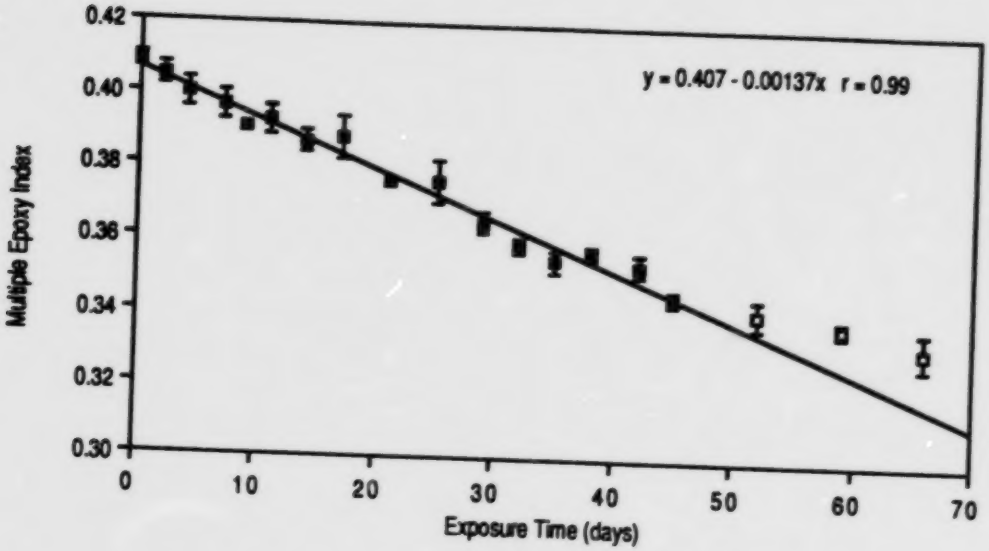


Figure 15. Variation of multiple epoxy index (as measured by IR transmission) as a function of prepreg exposure time. Unfilled squares were not included in regression analysis (see text).

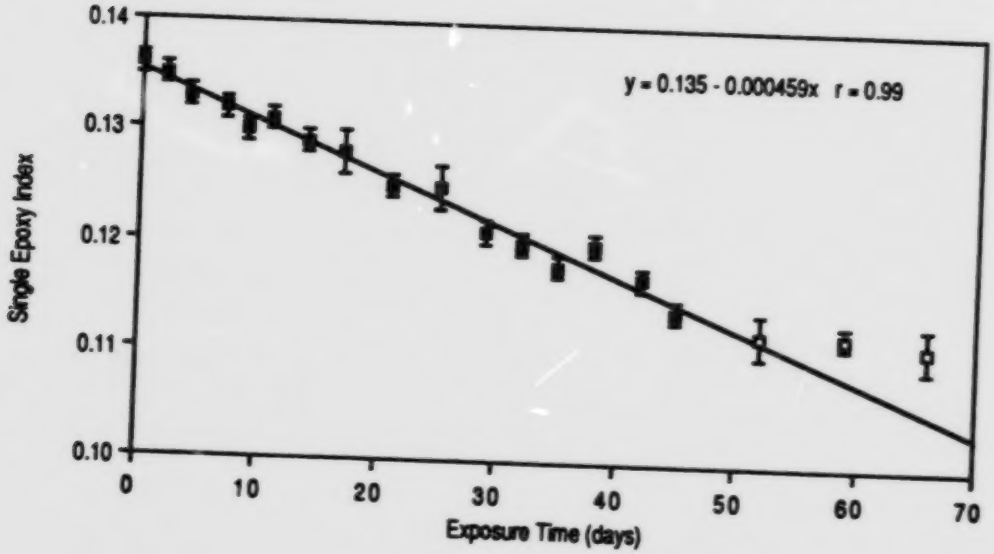


Figure 16. Variation of single epoxy index (as measured by IR transmission) as a function of prepreg exposure time. Unfilled squares were not included in regression analysis.

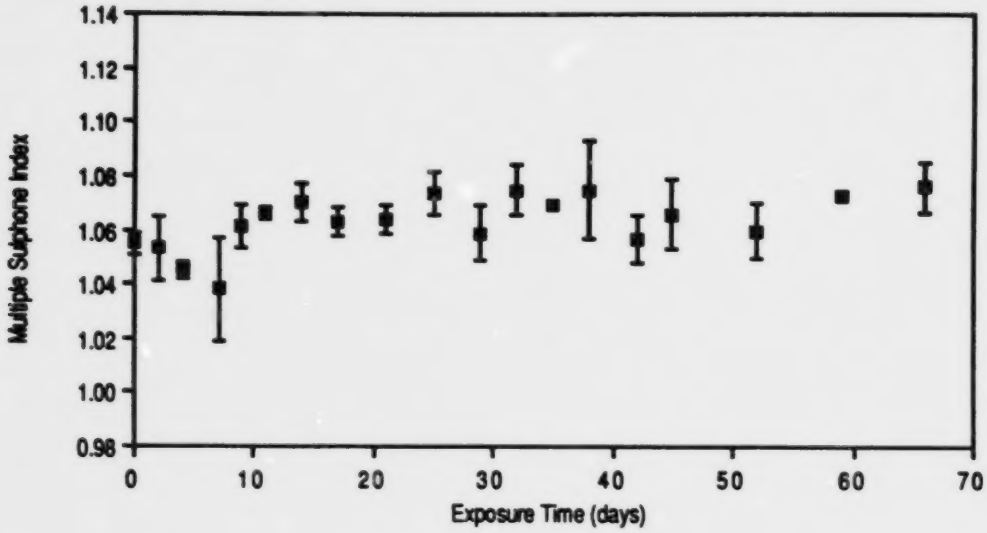


Figure 17. Variation of multiple sulphone index (as measured by IR transmission) as a function of prepreg exposure time.

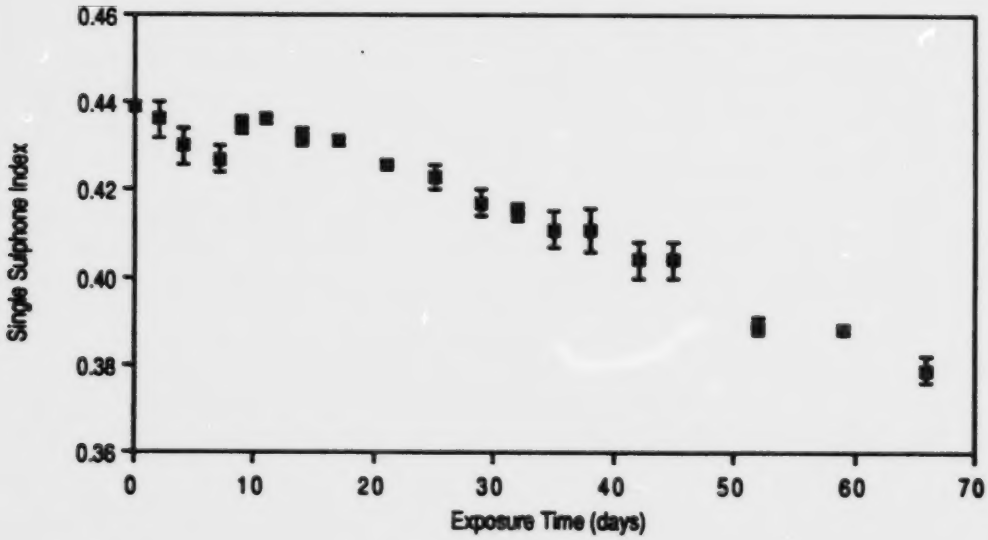


Figure 18. Variation of single sulphone index (as measured by IR transmission) as a function of prepreg exposure time.

There is little data in the literature for comparison. As already mentioned, Scola [15] studied the aging of Hercules 3501 by IR, but scatter in the data made it difficult to interpret the results. However, at 93% R.H. a definite downward trend is evident. The high degree of scatter may be due to errors resulting from variations in sample film thickness. As reported earlier [2], we have found that it is very important to have films of uniform thickness in order to obtain reproducible quantitative data. In the present work, care was taken to obtain films as uniform as possible, and as can be seen from Figures 15 and 16, this gives data with sufficient precision to be able to acceptably characterize the extent of prepreg aging.

Figures 17 and 18 show the behaviour of the sulphone indices. Ideally these should not change, since the sulphone groups are not destroyed by the curing reaction. However, they do vary with aging time, especially the single sulphone index, which decreases by about 0.2% per day. The reason for this is not clear, but it has been pointed out that the sulphone band intensities are affected by the transformation from primary to secondary amine upon reaction with epoxy [31, 32], as well as by the presence of moisture [33]. The aromatic band could also be sensitive to such effects. The multiple sulphone index appears to be less affected than the single sulphone index, so the former is preferred as an indicator of the total amount of hardener present. The variation is of the order of 3 to 4%, as compared to 14% for the single sulphone index.

4.2 ATTENUATED TOTAL REFLECTION

This method is described in Section 2.3.3.2. For this work, only selected samples from the aging study were run, since the object was not to obtain a complete set of data as in the transmission experiment, but rather to compare the two methods. Samples were measured using two different prisms, KRS-5 (thallium bromoiodide) and germanium. In the case of the KRS-5 prism, spectra were recorded both for "prepreg" (i.e. with the prepreg in contact with the prism) and for "residue" (i.e. the resin left on the prism after the prepreg was removed). Figure 19 compares the spectra recorded with a germanium prism for the fresh prepreg and the sample aged for 66 days. There are obvious changes in the shape of the N-H bands (3600-3100 cm^{-1}), the C-H bands (3100-2800 cm^{-1}), and the band near 1600 cm^{-1}, as well as an increase in the intensity of the peak at 1320 cm^{-1}. Also noticeable in the spectrum of the fresh prepreg is the acetone peak near 1710 cm^{-1}, which is absent from the spectrum of the aged prepreg.

The results of the quantitative analysis calculations are given in Table 5. In the case of the KRS-5 prism, they are of little value for characterizing the extent of aging. Firstly, except for the "Control" sample, there is a discrepancy between the values obtained for the "Prepreg" and for the "Residue". This is because as the prepreg ages, the resin becomes

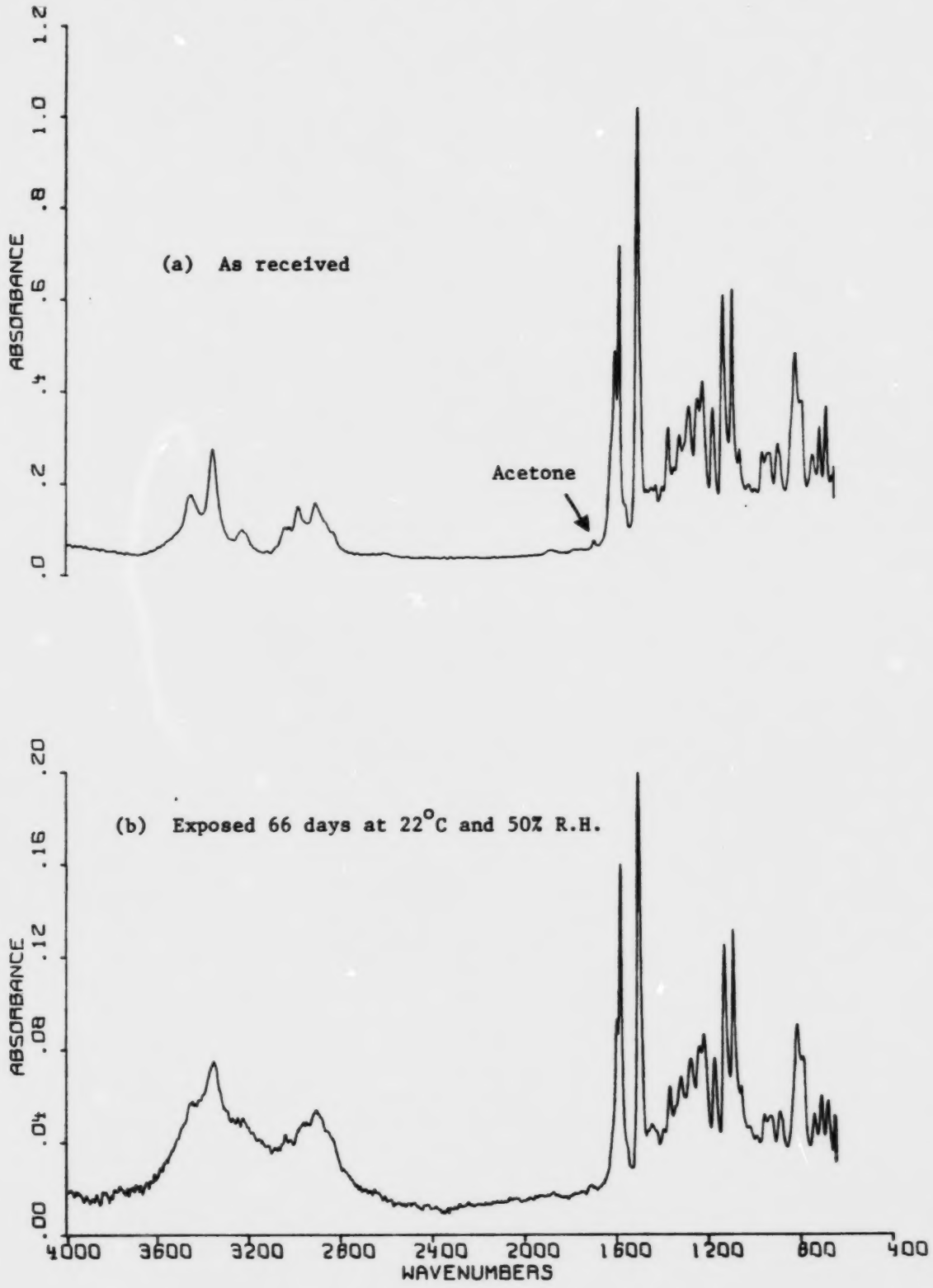


Figure 19. Attenuated total reflection IR spectra of Narmco 5208/WC3000 prepreg.

Table 5. Infrared spectroscopy results (attenuated total reflectance).

Sample	Prism	Nature of sample	Single epoxy index		Multiple epoxy index		Single sulphone index		Multiple sulphone index	
			Value	SD	Value	SD	Value	SD	Value	SD
Control	KRS-5	Prepreg	0.352	0.017	1.051	0.054	0.592	0.004	1.894	0.032
		Residue	0.345	0.019	1.030	0.059	0.586	0.004	1.865	0.038
14	KRS-5	Prepreg	0.351	0.032	1.059	0.085	0.623	0.017	2.012	0.054
		Residue	0.293	0.017	0.890	0.058	0.572	0.022	1.812	0.077
66	KRS-5	Prepreg	0.347	0.014	1.014	0.034	0.597	0.027	2.041	0.092
		Residue	0.259	0.019	0.762	0.053	0.535	0.014	1.728	0.098
Control	Ge	Prepreg	0.233	0.002	0.672	0.005	0.555	0.002	1.480	0.010
14	Ge	Prepreg	0.226	0.001	0.646	0.005	0.554	0.001	1.505	0.004
42	Ge	Prepreg	0.206	0.002	0.594	0.002	0 545	0.006	1.570	0.026
66	Ge	Prepreg	0.183	0.004	0.506	0.021	0.513	0.003	1.593	0.033

more viscous, and the amount of residue left on the prism is lower. The evanescent wave of the infrared beam then penetrates beyond the layer of resin into the surrounding air, and is effectively sampling both resin and air. This results in an artificially low index. Secondly, even when only the "Prepreg" results are considered, the standard deviations are large in comparison to the changes observed for the indices. This is due to the fact that there are band distortions resulting from refractive index effects, because the refractive index of the resin is close to that of the prism. Both these problems are discussed in more detail in an earlier report [2]. The results obtained here provide further confirmation of the findings reported there.

The germanium prism gives much better results. The higher refractive index of germanium means that the refractive index problem is much less important. The standard deviations are much lower, and the decrease in epoxy index with aging time can easily be seen. The results are plotted in Figures 20 to 23. Linear regression for the multiple and single epoxy indices gives lines whose slopes correspond to decreases of 0.36% and 0.32% per day respectively. These are very close to the value of 0.34% obtained by transmission. The sulphone indices also vary in much the same way as in transmission, although the variation for the multiple sulphone index seems to be somewhat higher. It should be noted that the actual values of the indices obtained are different in transmission and in ATR because of a wavelength dependence in the latter case [2].

Attenuated total reflectance with a germanium prism is probably the best IR method overall for characterizing Narmco 5208 graphite-epoxy prepreg. Although the precision is slightly poorer than in a carefully performed transmission experiment, it has the important advantage of not requiring solvent extraction of the prepreg and preparation of thin cast films. This saves time and avoids the problem of nonuniform film thickness. The prepreg can be measured as is, even if it has polymerized beyond the point where it is soluble in acetone. In addition, as mentioned above, the presence of acetone in the prepreg can be detected.

4.3 DIFFUSE REFLECTION

Three samples from the study (0, 7, and 14 days) were also examined by diffuse reflectance IR. For each sample, five specimens were measured and the spectra converted to both Kubelka-Munk and absorbance units. Epoxy and sulphone indices were calculated in the usual way, and the average results, together with standard deviation, are given in Table 6. In general, the standard deviation is large in comparison to the changes observed, so that this method is of no use for monitoring the prepreg aging. The reasons for the poor performance of diffuse reflectance as a quantitative technique are discussed in an earlier report [2].

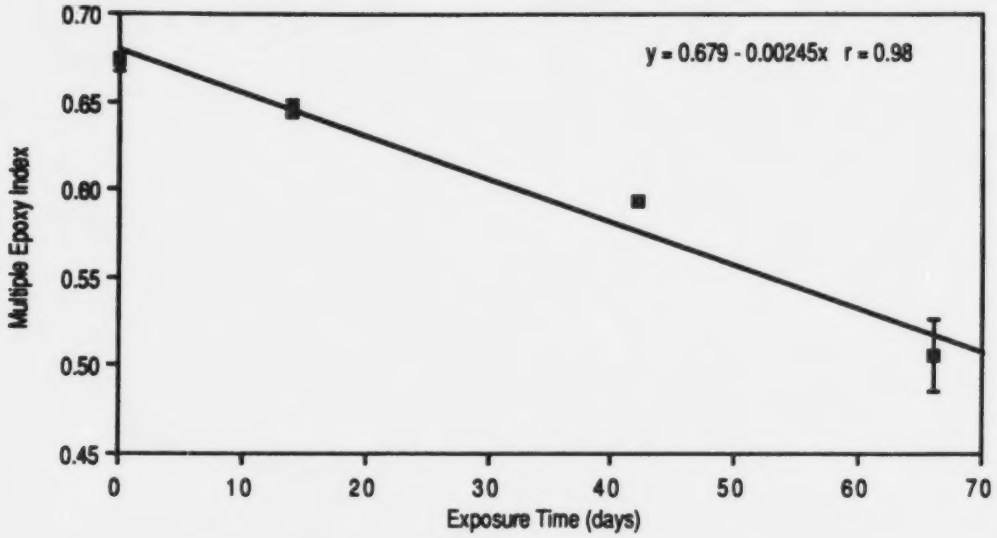


Figure 20. Variation of multiple epoxy index (as measured by IR attenuated total reflection) as a function of prepreg exposure time.

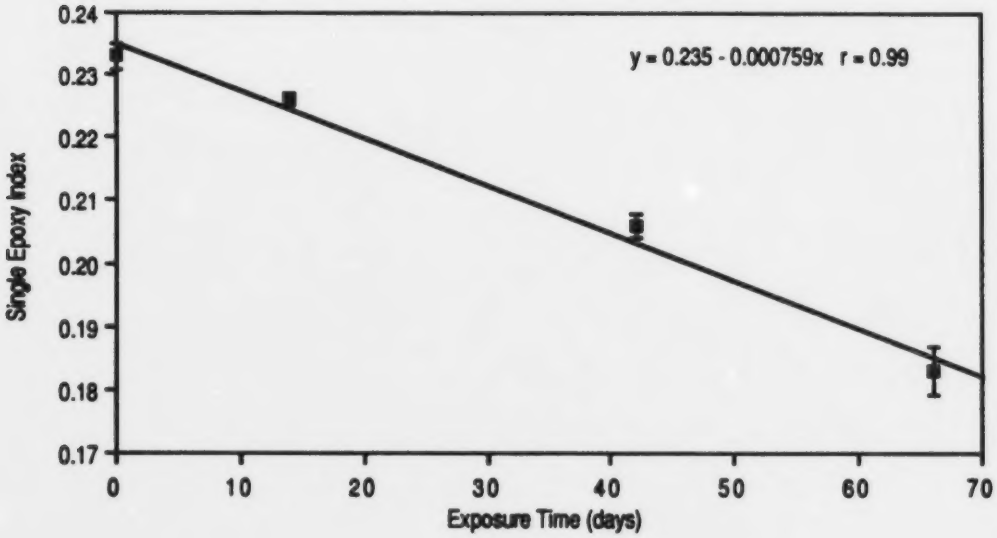


Figure 21. Variation of single epoxy index (as measured by IR attenuated total reflection) as a function of prepreg exposure time.

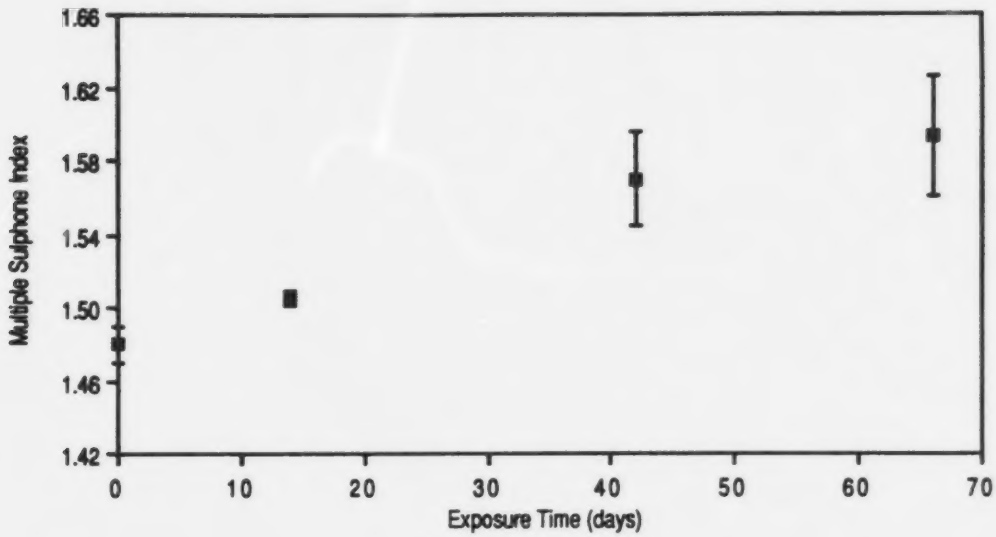


Figure 22. Variation of multiple sulphone index (as measured by IR attenuated total reflection) as a function of prepreg exposure time.

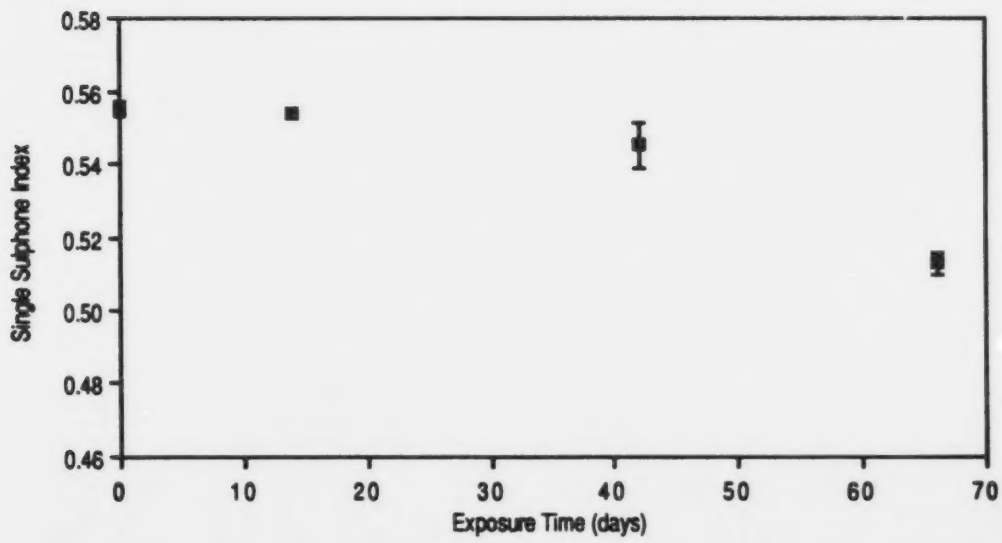


Figure 23. Variation of single sulphone index (as measured by IR attenuated total reflection) as a function of prepreg exposure time.

Table 6. Infrared spectroscopy results (diffuse reflectance).

Sample	Spectral units used	Single epoxy index		Multiple epoxy index		Single sulphone index		Multiple sulphone index	
		Value	SD	Value	SD	Value	SD	Value	SD
Control	K-M	0.175	0.024	0.539	0.072	0.377	0.032	1.068	0.086
7	K-M	0.195	0.037	0.597	0.112	0.417	0.030	1.144	0.114
14	K-M	0.171	0.042	0.537	0.139	0.373	0.056	1.070	0.150
Control	Abs	0.306	0.032	0.937	0.106	0.488	0.028	1.484	0.086
7	Abs	0.336	0.037	1.025	0.108	0.519	0.018	1.555	0.078
14	Abs	0.290	0.050	0.898	0.172	0.476	0.051	1.461	0.132

5. LIQUID CHROMATOGRAPHY

5.1 REVERSE-PHASE LIQUID CHROMATOGRAPHY (RPLC)

Reverse-phase liquid chromatography was done according to the method developed as described in an earlier report [3] and outlined in Section 2.3.3.4. A typical chromatogram is shown in Figure 24. Nine different peaks were treated quantitatively using both area and height. The results were expressed both in terms of the normalized peak area or height with respect to the acetophenone internal standard, and in terms of the ratio with respect to the TGDDM peak. For each sample, two separate specimens were extracted, and for each extraction, three injections were performed. The results from the three injections were used to calculate an average and a standard deviation for each of the two extractions. This procedure generated a large amount of data which is given in Appendix A and shown graphically in figures to be discussed shortly. To give a general idea of the results obtained, selected data are given in Table 7. For each sample, the two extractions are averaged to give a single value. Results are given for the four most important peaks of the chromatogram: DDS (peak 1), TGDDM-DDS reaction product (peak 7), TGDDM (peak 9), and DGEBA (peak 10). Both the normalized area with respect to acetophenone and the area ratios with respect to TGDDM are shown. The various peaks analysed will be discussed individually.

5.1.1 Peak 1 (DDS)

The variation of peak 1, which corresponds to unreacted amine hardener diaminodiphenylsulphone, is shown in Figure 25. For each exposure time there are two points corresponding to the two different extractions. The error bars correspond to the calculated standard deviations based on the average of three injections. Both the actual amount of free DDS, as represented in the upper graph, and the ratio of DDS to TGDDM, as represented in the lower graph, show a linear decrease with exposure time. The degree of scatter is considerably less when the peak area is used rather than the peak height. This is because this particular peak sometimes shows resolved structure, depending on RPLC column conditions, and when this happens the measured height is affected more than the area [3]. Hence it is preferable to use area for the calculation. Linear regression of the area data gives the following equations, with a correlation coefficient of 0.99:

$$\text{Normalized area} = 4.04 - 0.0424 \times (\text{number of days exposure})$$

$$\text{Peak ratio w.r.t. TGDDM} = 0.316 - 0.0027 \times (\text{number of days exposure}).$$

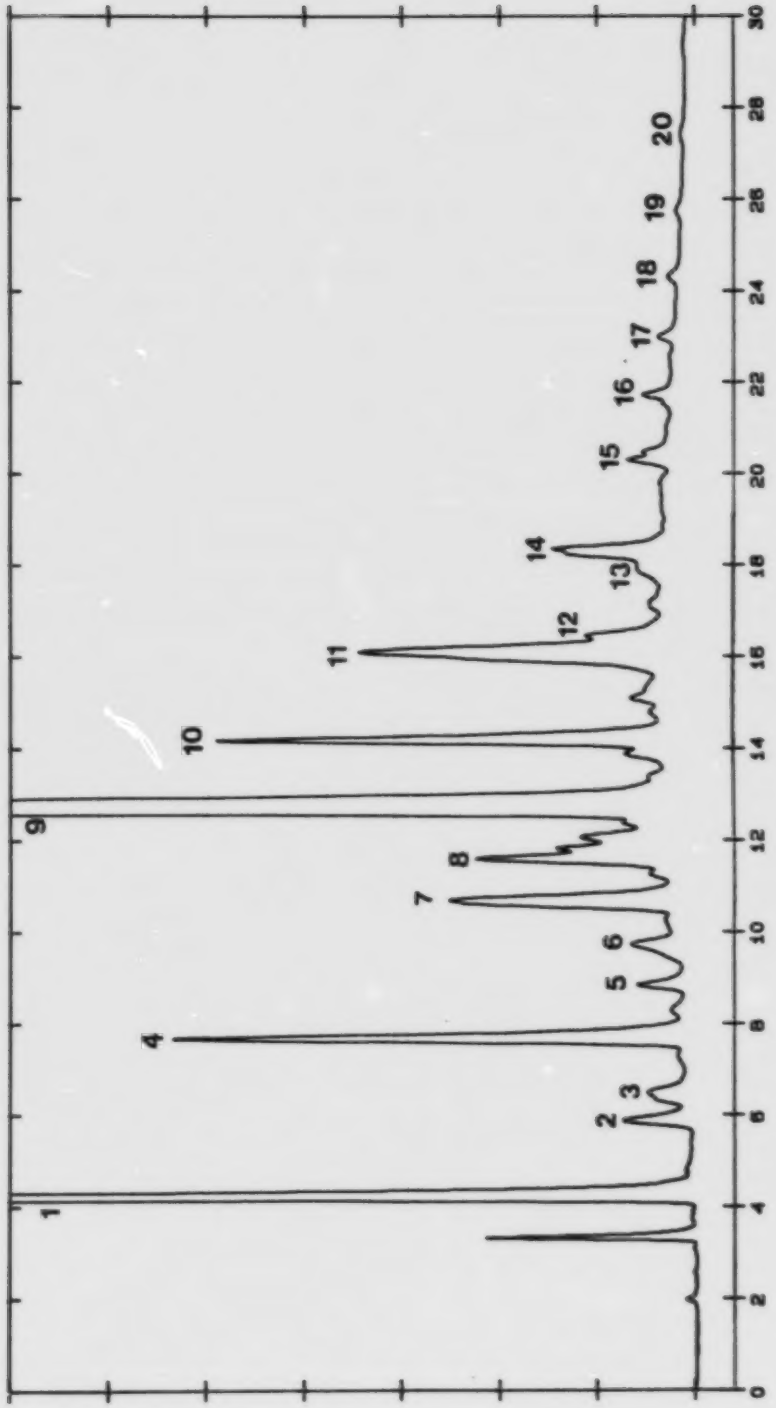


Figure 24: RPLC chromatogram of Narmco 5208 prepreg (THF extract)

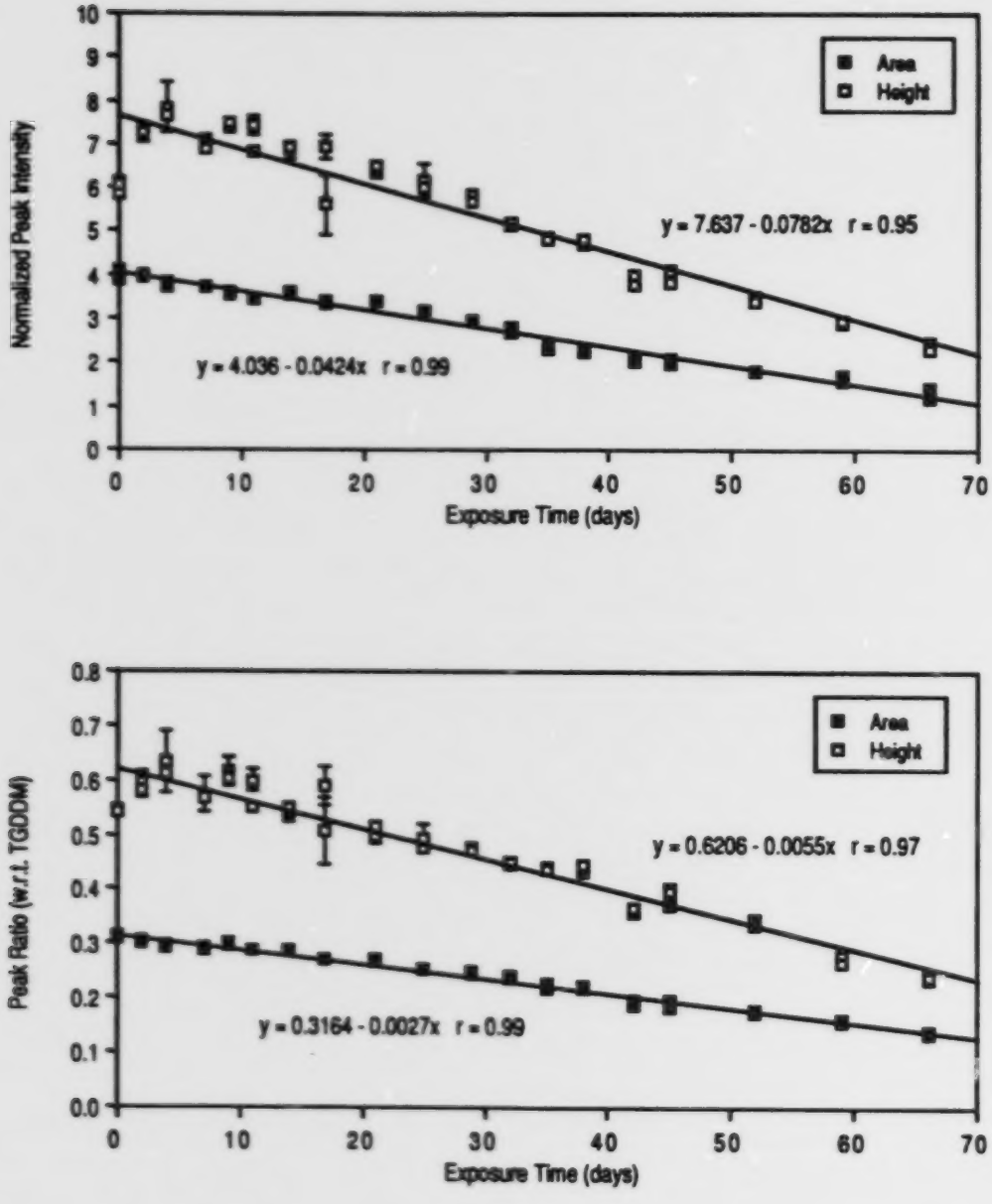

Normalized Peak Intensity
Area
Height
y = 7.637 - 0.0782x r = 0.95
y = 4.036 - 0.0424x r = 0.99
Exposure Time (days)
Peak Ratio (w.r.t. TGDDM)
Area
Height
y = 0.6206 - 0.0055x r = 0.97
y = 0.3164 - 0.0027x r = 0.99
Exposure Time (days)

Figure 25. Variation of RPLC peak 1 (DDS) as a function of prepreg exposure time, expressed in terms of normalized intensity with respect to acetophenone internal standard (upper graph) or in terms of the ratio with respect to the TGDDM peak (lower graph)

The calculated slope shows that the amount of free DDS decreases at a rate of 1.02% per day, based on the initial value. The ratio DDS/TGDDM decreases at a slightly lower rate (0.85%) because the amount of TGDDM decreases concurrently with the DDS.

Table 7. RPLC results (based on peak areas) for major peaks.

Sample	Normalized area (w.r.t. ACP)				Area ratio (w.r.t. TGDDM)		
	Peak 1 (DDS)	Peak 7 (RP)	Peak 9 (TGDDM)	Peak 10 (DGEBA)	Peak 1 (DDS)	Peak 7 (RP)	Peak 10 (DGEBA)
Control	3.993	1.426	12.77	1.583	0.3128	0.1117	0.1239
2	3.988	1.504	12.59	1.473	0.3047	0.1149	0.1126
4	3.787	1.589	12.82	1.459	0.2953	0.1239	0.1138
7	3.716	1.600	12.81	1.485	0.2901	0.1249	0.1159
9	3.568	1.557	12.06	1.397	0.2988	0.1304	0.1171
11	3.457	1.584	11.96	1.367	0.2890	0.1324	0.1142
14	3.595	1.786	12.52	1.454	0.2872	0.1427	0.1162
17	3.365	1.759	12.41	1.349	0.2711	0.1417	0.1087
21	3.388	2.000	12.66	1.394	0.2677	0.1580	0.1101
25	3.159	2.039	12.37	1.320	0.2554	0.1648	0.1067
29	2.962	2.062	11.99	1.254	0.2471	0.1720	0.1046
32	2.741	1.996	11.55	1.134	0.2373	0.1729	0.0981
35	2.345	1.780	10.51	1.071	0.2231	0.1694	0.1019
38	2.250	1.772	10.22	0.965	0.2202	0.1734	0.0944
42	2.057	1.871	10.59	0.935	0.1942	0.1766	0.0882
45	2.023	1.864	10.71	0.929	0.1889	0.1741	0.0868
52	1.805	1.825	10.30	0.829	0.1754	0.1773	0.0804
59	1.638	1.820	10.30	0.801	0.1591	0.1767	0.0776
66	1.335	1.859	9.77	0.655	0.1366	0.1899	0.0670
50D	2.351	1.914	11.48	1.112	0.2048	0.1668	0.0969
87F	4.037	1.494	13.07	1.681	0.3091	0.1143	0.1286

5.1.2 Peak 7 (Reaction Product "RP")

This peak corresponds to the product of reaction of one molecule of TGDDM with one molecule of DDS. The variation is shown in Figure 26. Initially the amount increases, but after about 30 days it reaches a plateau and subsequently begins to decrease, as the product undergoes further reaction with TGDDM or DDS to produce molecules of higher molecular weight. In this case, the use of peak height gives somewhat less scatter. This is

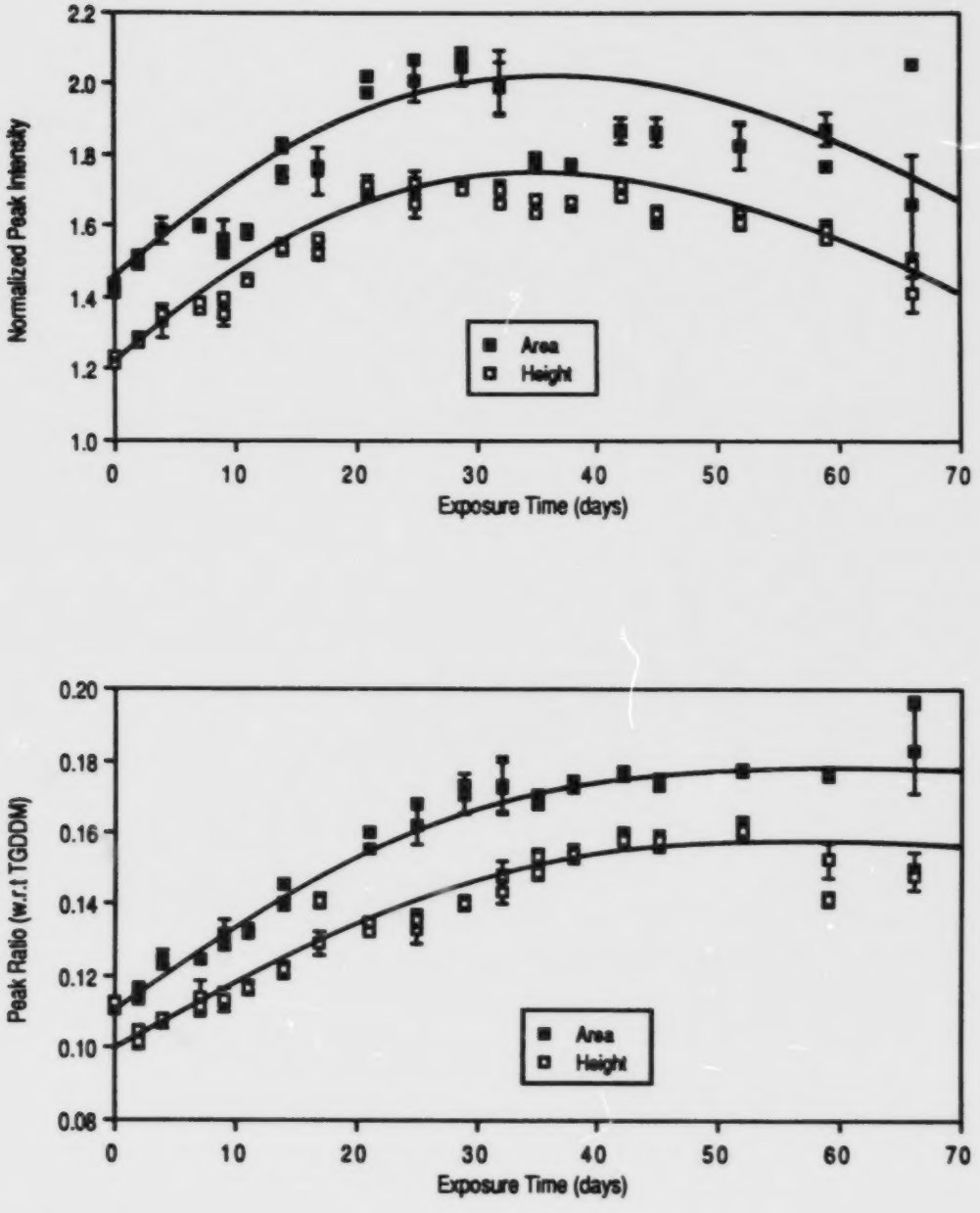


Figure 26. Variation of RPLC peak 7 (TGDDM-DDS reaction product) as a function of prepreg exposure time.

probably due to overlap with some weaker peaks, in which case the degree of peak resolution will affect the calculation, more so for peak area than for height. The ratio RP/TGDDM increases up to about 30 days and then remains steady as both RP and TGDDM decrease together.

5.1.3 Peak 8

The compound responsible for this peak has not been identified, but it has been established that it arises from the major epoxy. It is included in the analysis because it is one of the stronger peaks in the chromatogram. As seen in Figure 27, it shows no significant change over the course of the aging experiment. Like peak 7, it overlaps some weaker peaks, so the results calculated using peak height show less scatter.

5.1.4 Peak 9 (TGDDM)

The TGDDM peak is the strongest in the chromatogram. As shown in Figure 28, it gradually decreases with exposure time. The degree of scatter is about the same whether area or height is used, and appears to be somewhat higher than for the DDS peak. Linear regression (using the area results) gives the following equation, corresponding to a decrease in TGDDM content of 0.38% per day, based on the initial value:

$$\text{Normalized area} = 12.95 - 0.0493 \times (\text{number of days exposure}).$$

5.1.5 Peak 10 (DGEBA)

This peak is due to DGEBA, or diglycidyl ether of bisphenol A, the main component of the minor epoxy resin (based on bisphenol A Novolac). Like DDS and TGDDM, it shows a linear decrease with exposure time (Figure 29). Data based on peak area show less scatter than those based on peak height. Linear regression (using the area data) gives the following equations:

$$\text{Normalized area} = 1.57 - 0.0137 \times (\text{number of days exposure})$$

$$\text{Peak ratio w.r.t. TGDDM} = 0.123 - 0.000766 \times (\text{number of days exposure}).$$

The first equation shows that the amount of DGEBA decreases at a rate of 0.87% per day. This is more than twice the rate for TGDDM, so as a result the ratio DGEBA/TGDDM also decreases with time.

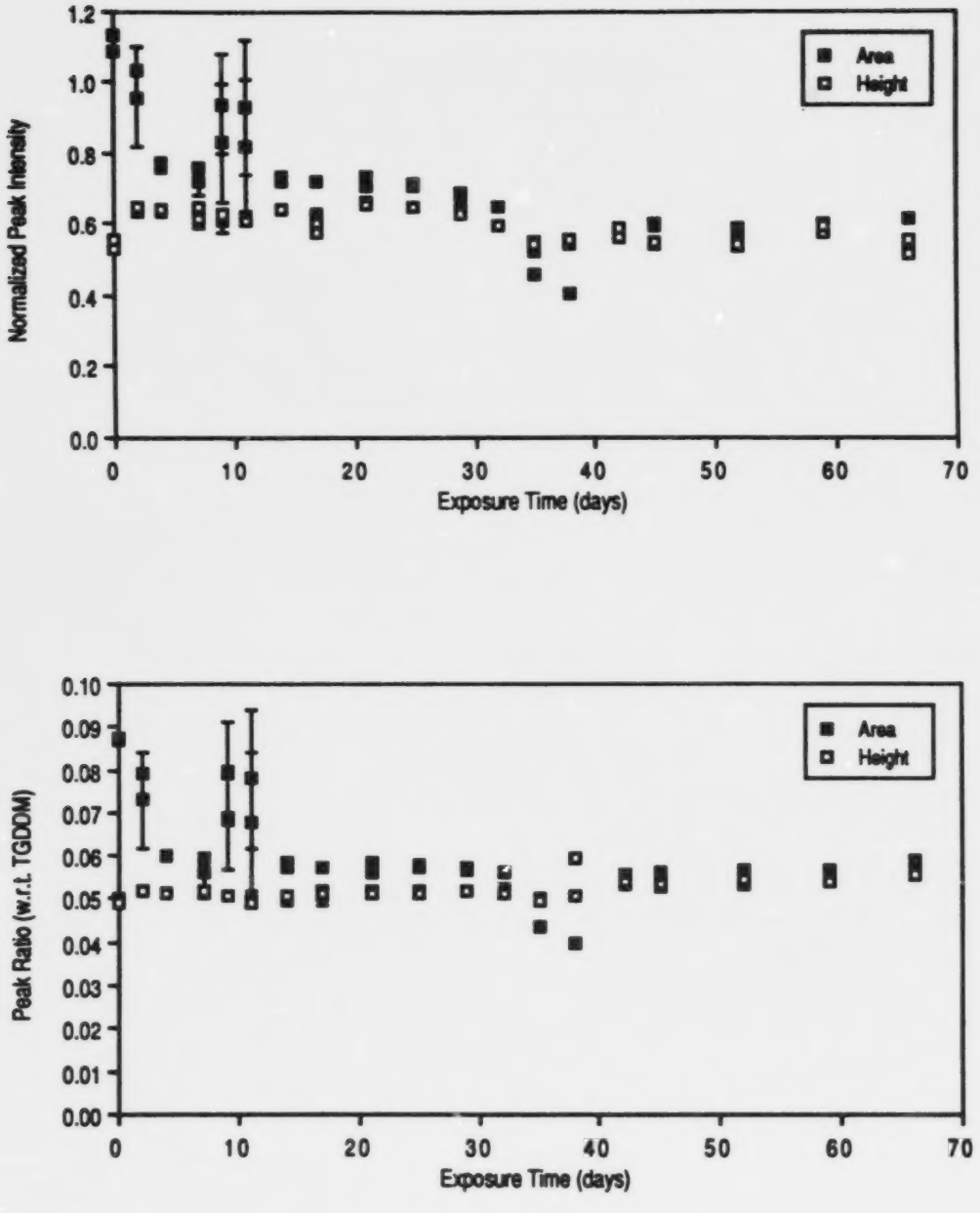


Figure 27. Variation of RPLC peak 8 as a function of prepreg exposure time.

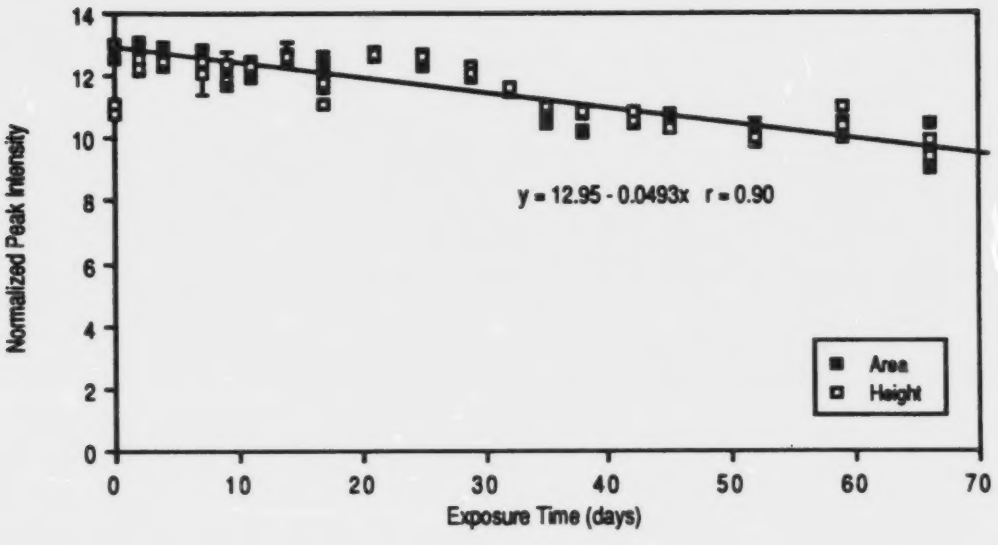


Figure 28. Variation of RPLC peak 9 (TGDDM) as a function of prepreg exposure time.

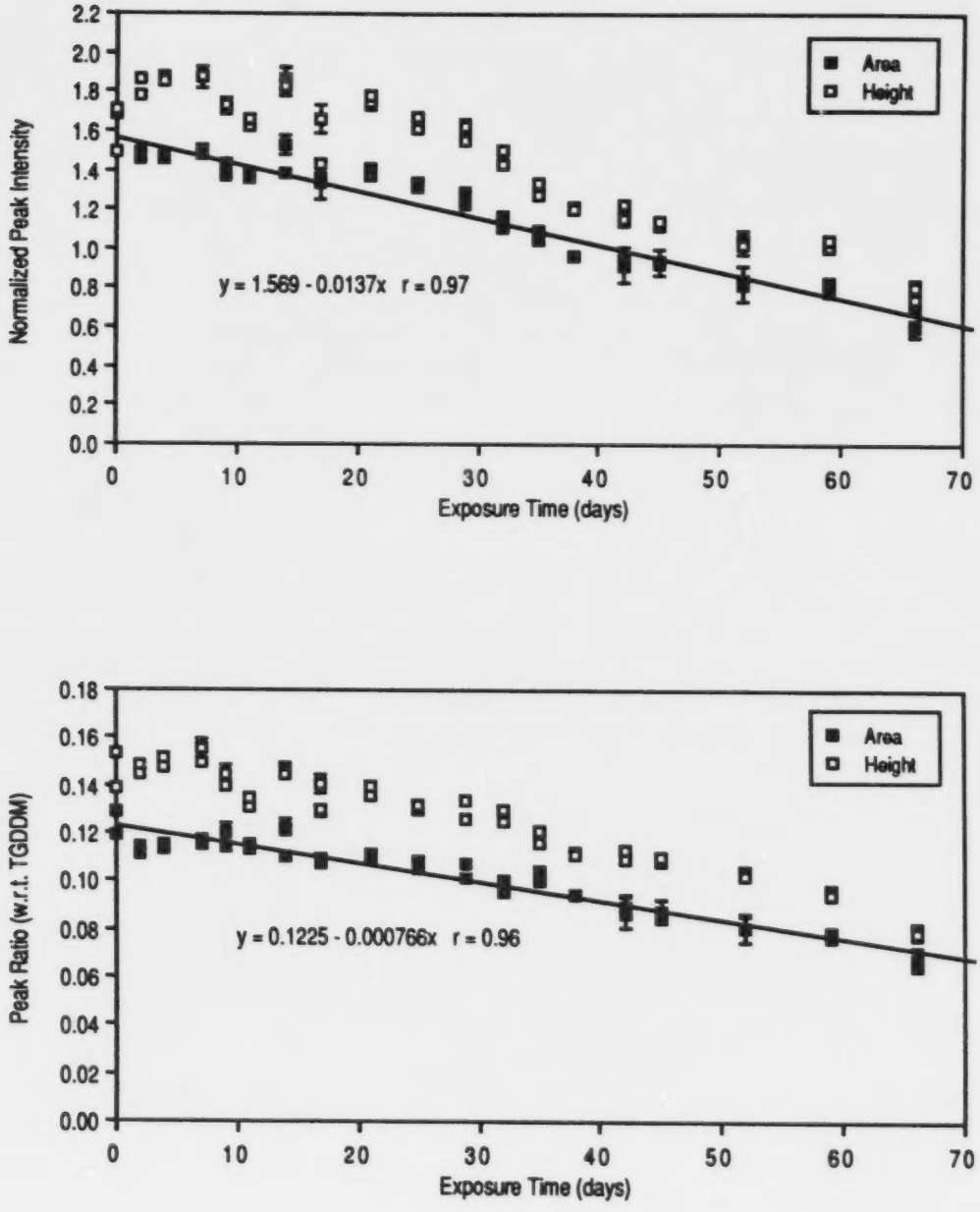


Figure 29. Variation of RPLC peak 10 (DGEBA) as a function of prepreg exposure time.

5.1.6 Peak 11

This peak corresponds to a higher-molecular-weight component of the TGDDM-based resin. It too decreases with time, at a rate of 0.96% per day, as shown in Figure 30. The use of peak height gives less scatter than peak area, because of interference from peak 12. Unlike peak 8, which also comes from the major epoxy, peak 11 changes with aging time, so it appears to be related to a reactive component of the system and not an inert impurity or by-product.

5.1.7 Peaks 14, 15, 16

These three relatively small peaks are probably due to high-molecular-weight oligomers of the Novolac resin. Their variation is shown in Figures 31, 32, and 33. All three decrease with time. Linear regression, based on the data calculated using peak height, gives rates of decrease of 0.72%, 0.87%, and 1.00% per day, respectively.

5.1.8 Discussion

Most of the distinct peaks in the RPLC chromatogram show a linear decrease with respect to the time of prepreg exposure. The main exception is peak 7, the reaction product peak, which increases up to about 30 days and then decreases.

The peak which is most sensitive to the prepreg aging is peak 1, the DDS peak, which decreases at a rate of about 1% per day. However, a low value for this peak is not necessarily indicative of resin advancement, since it could be due to a low content of DDS in the initial formulation. It can only be used to check resin advancement if it is used in conjunction with other data. For instance, if a value has been determined for the same batch immediately after it was produced, comparison of the two will indicate whether reaction has occurred. Likewise, if the total content of DDS is known to be normal from infrared analysis (sulphone index), then an unusually low content of free DDS (RPLC peak 1) indicates that resin advancement has occurred. A better "absolute" indicator of the degree of advancement is the reaction product peak, since there is none of this compound in the starting materials. However, the relative error associated with measurement of this peak appears to be higher than for the DDS peak.

It is interesting to note that the rate of decrease is considerably lower for TGDDM than for DGEBA. If both molecules were equally reactive, one would expect the TGDDM to disappear at the same rate as the DGEBA, or even faster, because it has more epoxy

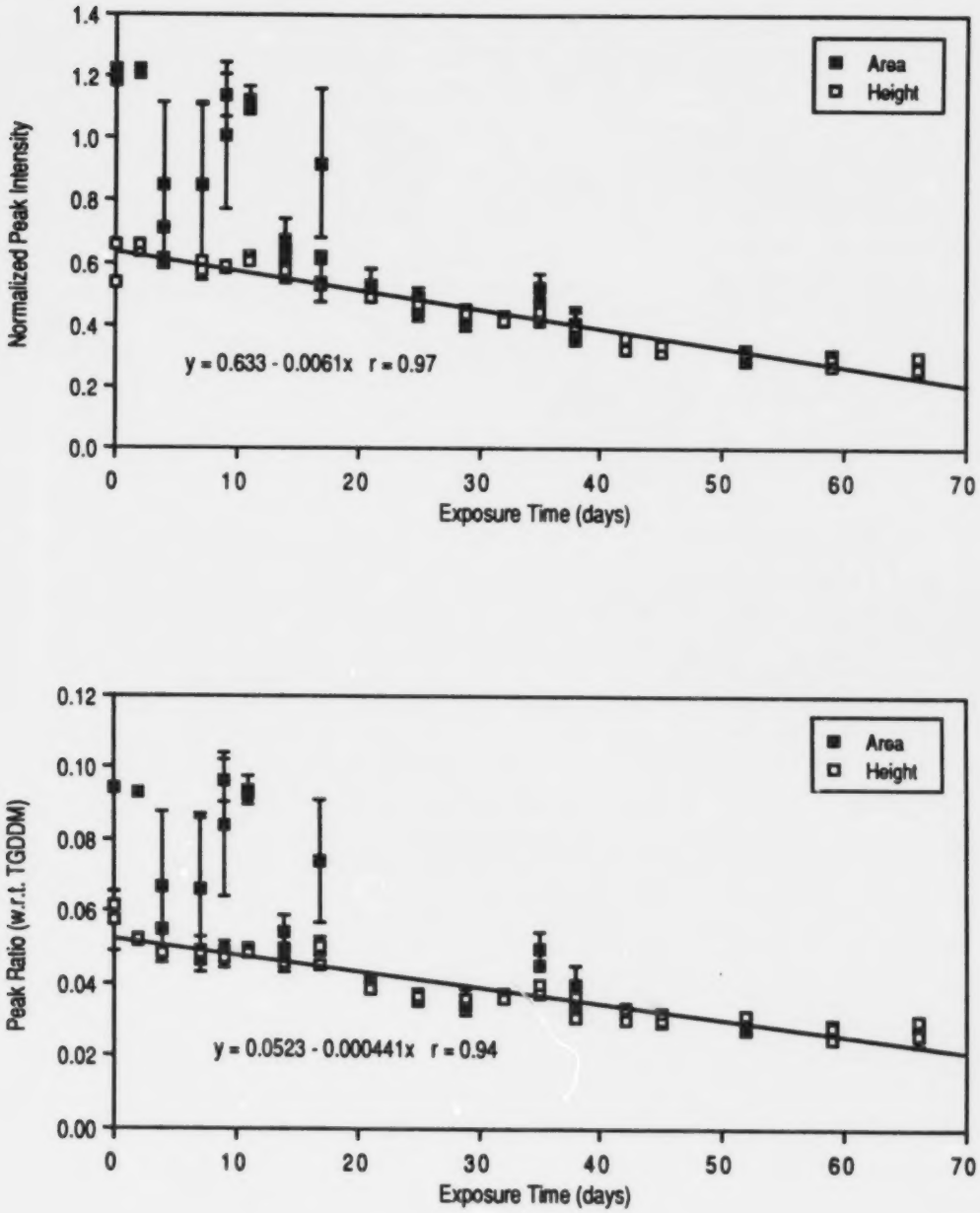


Figure 30. Variation of RPLC peak 11 as a function of prepreg exposure time.

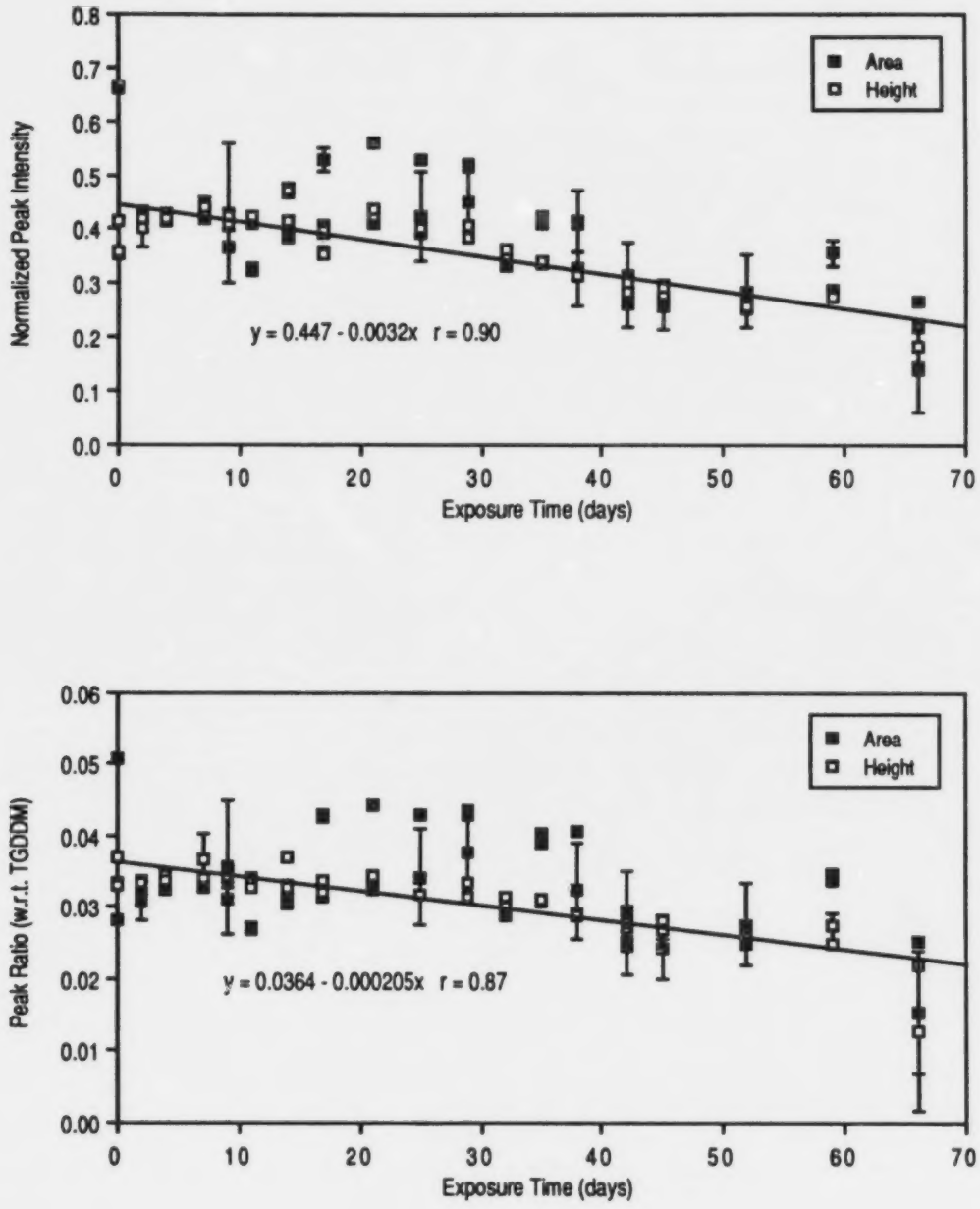


Figure 31. Variation of RPLC peak 14 as a function of prepreg exposure time.

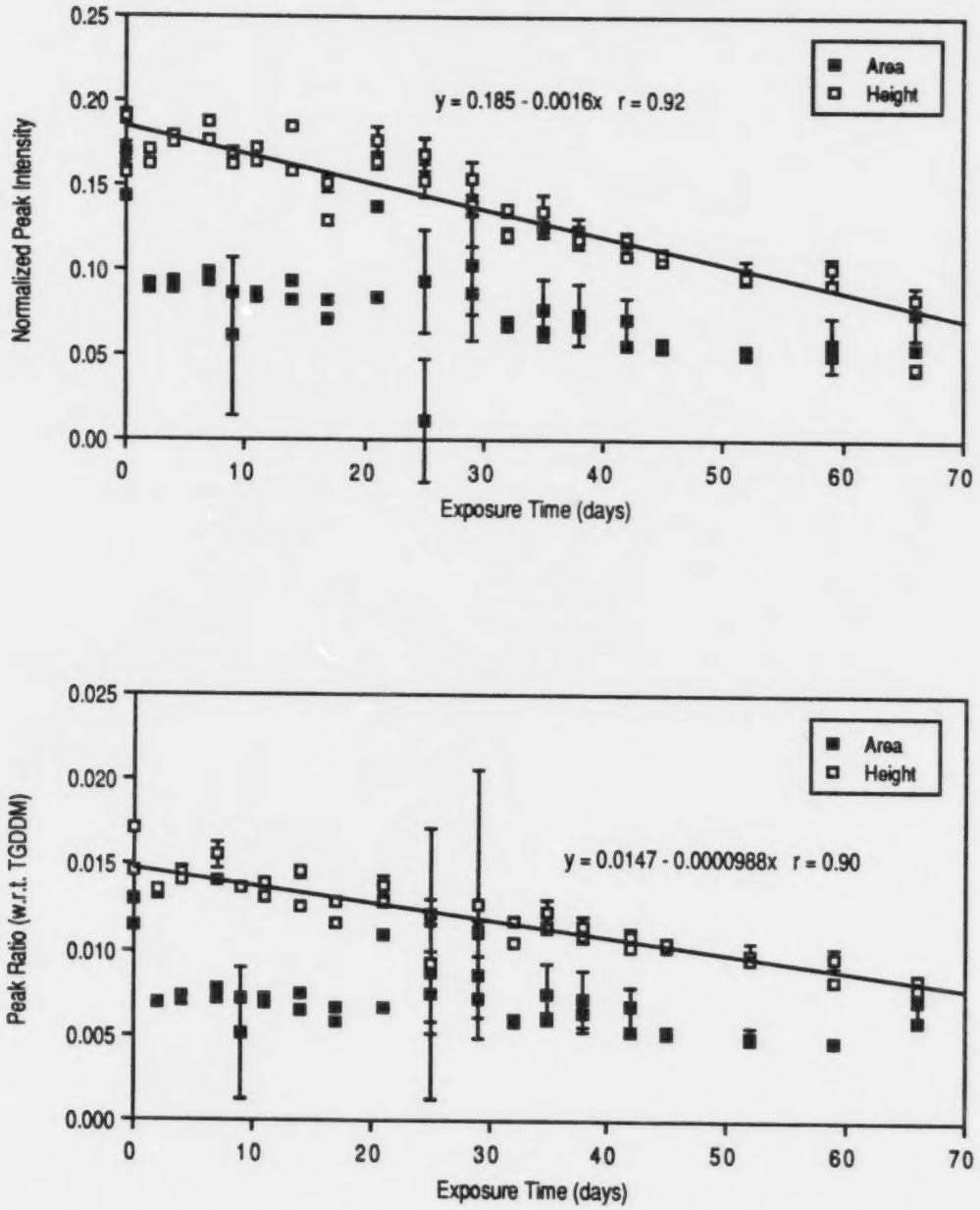


Figure 32. Variation of RPLC peak 15 as a function of prepreg exposure time.

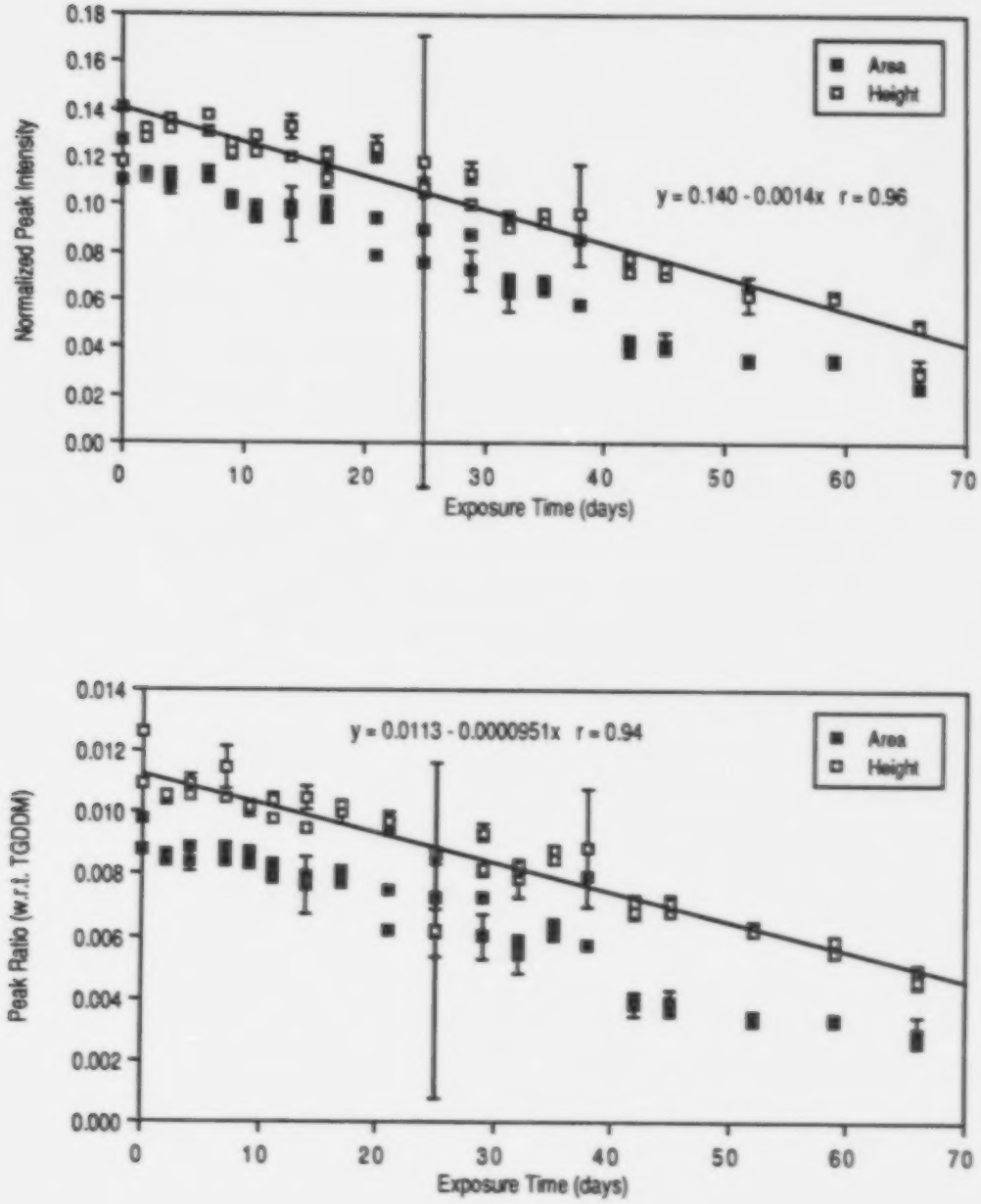


Figure 33. Variation of RPLC peak 16 as a function of prepreg exposure time.

groups per molecule. The results indicate that this is not the case, and that DGEBA appears to be more reactive than is TGDDM with respect to DDS hardener.

The results observed here may be compared in a general way with those found for similar systems in the past. For example, in his study of an unspecified TGDDM/DDS formulation aged at ambient temperature, May [13] found that over a 63-day period the content of DDS and TGDDM monomers dropped by 26% and 14% respectively. The corresponding figures in the present study are 66% and 24% for the same period. For Hercules 3501, after 40 days under dry conditions at ambient temperature, Sewell [14] found a drop in free DDS of 35%, compared with 42% in this work. Also with Hercules 3501, Hagnauer [12] found significant changes on aging at 22°C, especially during the first week, when the DDS and TGDDM dropped by 30% and 20% from their initial values. In the present study, a more gradual (linear) decrease was observed, with drops of only 7.4% and 2.7% respectively after one week. The discrepancies between the present results and the earlier ones cited may be explained in terms of variations in composition (minor epoxies, catalysts) and exposure conditions. Hinrichs and Thuen [7] have reported some results for the same system used here, Narmco 5208, but the duration of the experiment was only five days (75°F, 0% and 98% R.H.). They detected no significant changes over this period, probably because such changes were smaller than the error of measurement involved. The present study has shown that small changes do indeed occur, and can be detected if sufficiently sensitive methods are used.

5.2 HIGH-SPEED REVERSE-PHASE LIQUID CHROMATOGRAPHY (HS-RPLC)

By using columns packed with particles of diameter 3 μm rather than 5 μm or 10 μm, the time required for an RPLC analysis can be substantially reduced [3]. Five samples from the aging study were analysed by this method as described in Section 2.3.3.5. A typical chromatogram with peak identification is given in Figure 34. The results were calculated in the same way as in RPLC, but using only peak areas and not heights. They are summarized in Table 8. The values shown in parentheses correspond to the standard deviation of an average based on three injections. In the following discussion of the different peaks, the abbreviation RPLC refers to the use of a column 30 cm long packed with 5 μm particles, whereas HS-RPLC refers to a column 5 cm long packed with 3 μm particles.

5.2.1 Peak 1 (DDS)

The variation of the DDS peak, shown in Figure 35, is similar to that observed in RPLC. There is a continuous decrease with time and linear regression gives the following

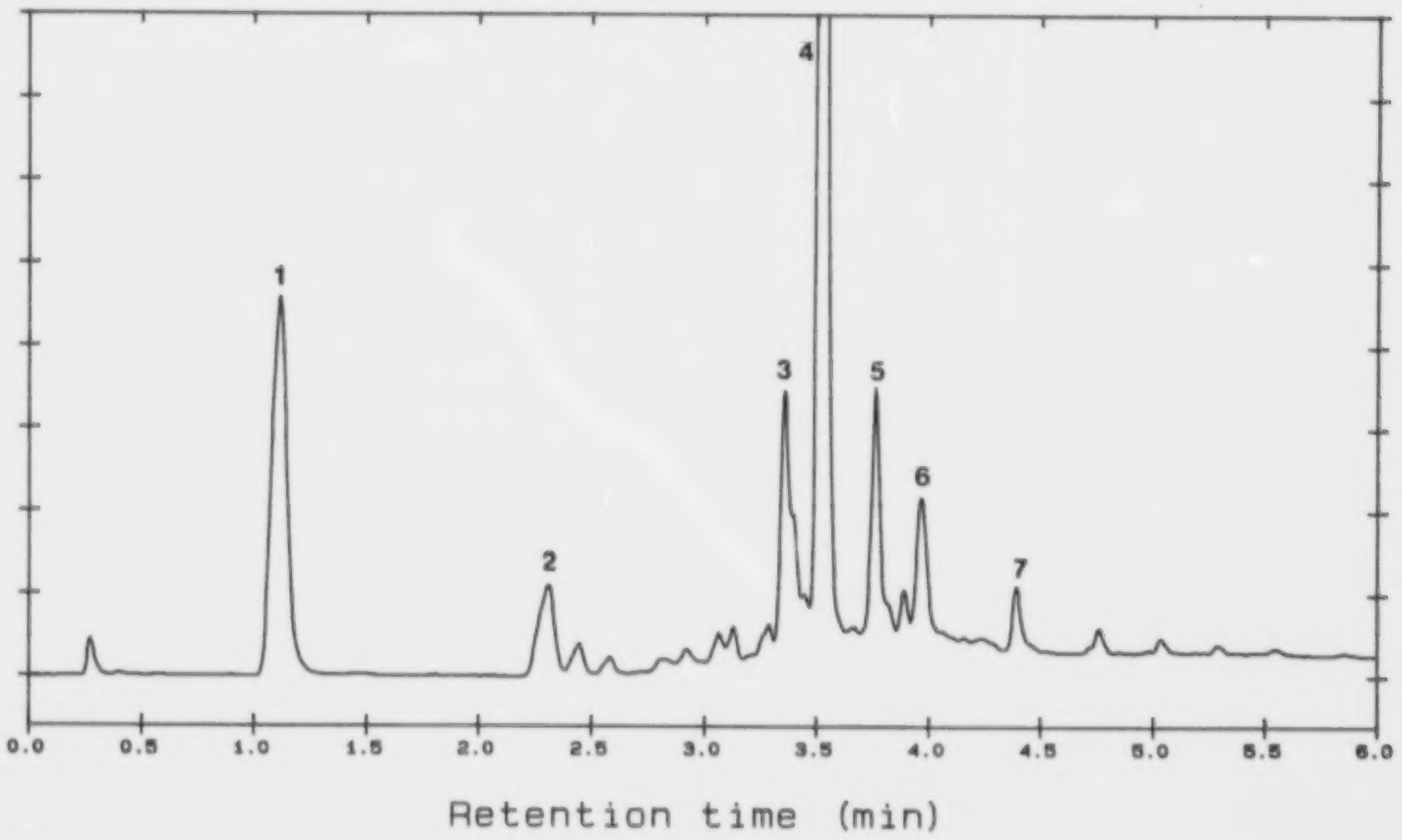


Figure 34: High-speed RPLC chromatogram of Narmco 5208 prepreg (THF extract)

Table 8. High-speed RPLC results.

Normalized peak areas with respect to acetophenone internal standard												
Sample	Peak 1 (DDS)		Peak 3 (Reaction Product)		Peak 4 (TGDDM)		Peak 5 (DGEBA)		Peak 6		Peak 7	
2	4.81	(0.12)	2.65	(0.26)	14.66	(0.83)	1.797	(0.054)	1.056	(0.076)	0.472	(0.014)
11	4.492	(0.086)	3.135	(0.059)	15.60	(0.30)	1.870	(0.020)	1.000	(0.017)	0.477	(0.009)
25	3.689	(0.083)	3.202	(0.046)	14.04	(0.21)	1.648	(0.035)	0.787	(0.015)	0.380	(0.013)
38	2.681	(0.036)	3.101	(0.024)	12.65	(0.11)	1.465	(0.006)	0.654	(0.016)	0.312	(0.007)
66	1.494	(0.013)	2.694	(0.010)	10.69	(0.06)	1.131	(0.016)	0.541	(0.005)	0.139	(0.026)

Peak area ratios with respect to TGDDM peak										
Sample	Peak 1 (DDS)		Peak 3 (Reaction Product)		Peak 5 (DGEBA)		Peak 6		Peak 7	
2	0.328	(0.011)	0.1804	(0.0077)	0.1226	(0.0033)	0.0720	(0.0011)	0.0322	(0.0009)
11	0.2880	(0.0007)	0.2010	(0.0003)	0.1199	(0.0010)	0.0641	(0.0005)	0.0306	(0.0006)
25	0.2626	(0.0024)	0.2279	(0.0006)	0.1173	(0.0008)	0.0560	(0.0006)	0.0270	(0.0009)
38	0.2119	(0.0011)	0.2450	(0.0006)	0.1158	(0.0009)	0.0517	(0.0013)	0.0246	(0.0008)
66	0.1398	(0.0004)	0.2521	(0.0006)	0.1058	(0.0009)	0.0506	(0.0002)	0.0130	(0.0025)

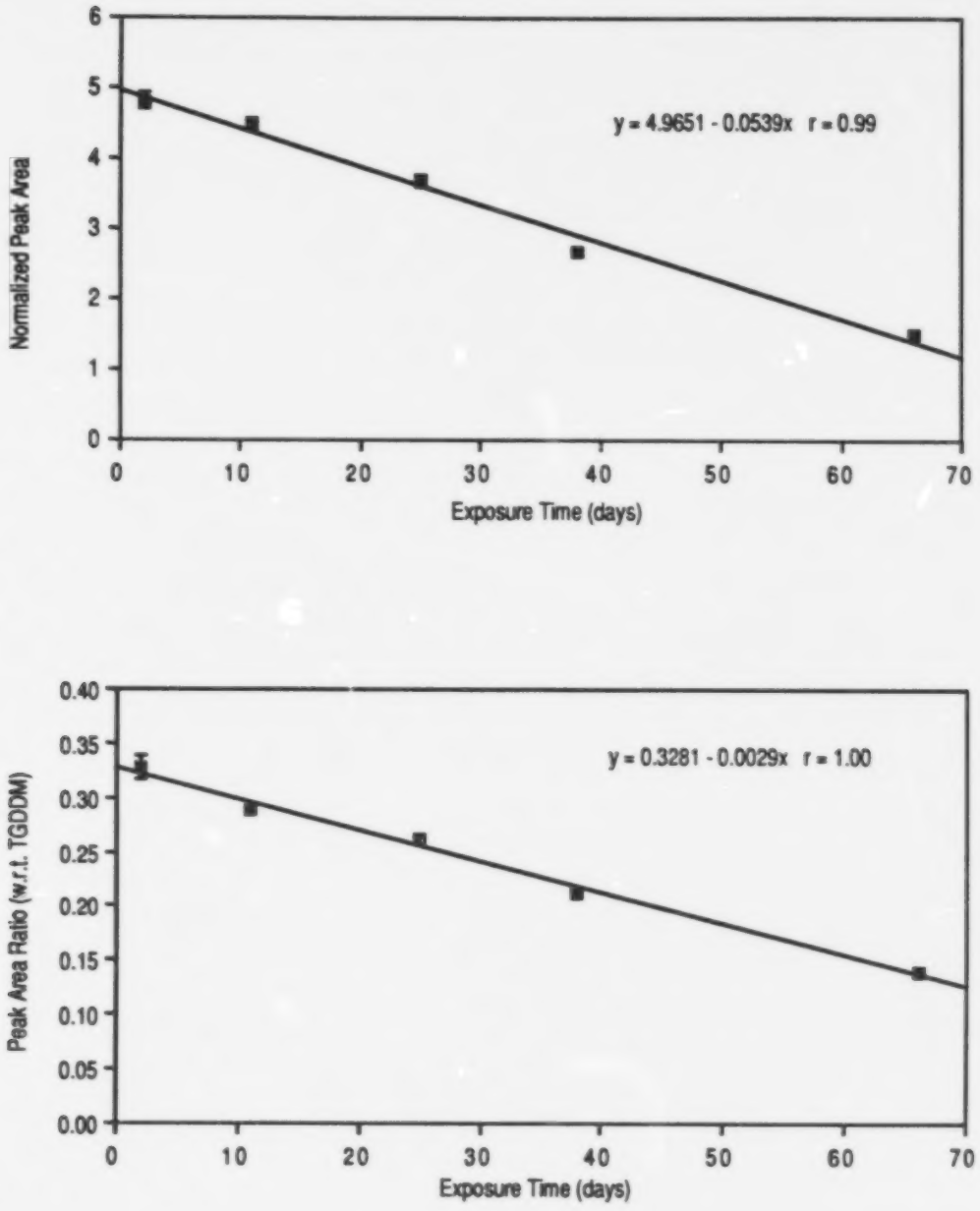

Normalized Peak Area
y = 4.9651 - 0.0539x r = 0.99
Exposure Time (days)
Peak Area Ratio (w.r.t. TGDDM)
y = 0.3281 - 0.0029x r = 1.00
Exposure Time (days)

Figure 35. Variation of HS-RPLC peak 1 (DDS) as a function of prepreg exposure time.

equations (correlation coefficient 0.99):

Normalized area = 4.97 - 0.054 x (number of days exposure)

Peak ratio w.r.t. TGDDM = 0.328 - 0.0029 x (number of days exposure).

Based on the normalized area, the amount of free DDS decreases at a rate of 1.09% per day, which compares very well with the value of 1.02% obtained with ordinary RPLC.

5.2.2 Peak 3 (Reaction Product "RP")

This peak corresponds to peak 7 in the RPLC chromatogram. Its variation is shown in Figure 36. The behaviour is much the same as that observed in RPLC, with a maximum occurring around 30 days. The RP/TGDDM ratio reaches a plateau at the same time.

5.2.3 Peak 4 (TGDDM)

As in RPLC (peak 9), the TGDDM monomer peak is the strongest in the chromatogram, and it varies in a similar manner (Figure 37). Linear regression gives the following equation (correlation coefficient 0.95):

Normalized area = 15.59 - 0.0727 x (number of days exposure).

The slope corresponds to a drop of 0.46% per day, compared to 0.38% in RPLC. The discrepancy may be due to the difference in peak resolution between the two methods. The measured peak area may involve contributions from other (minor) peaks which may not be the same in both cases.

5.2.4 Peak 5 (DGEBA)

This peak, corresponding to peak 10 in RPLC, shows a linear decrease with exposure time (Figure 38) which is similar to that observed in RPLC. Linear regression gives the following equations (correlation coefficients 0.98):

Normalized area = 1.909 - 0.0115 x (number of days exposure)

Peak ratio w.r.t. TGDDM = 0.123 - 0.000251 x (number of days exposure).

The rate of decrease in this case is 0.60% per day, compared to 0.87% per day in RPLC.

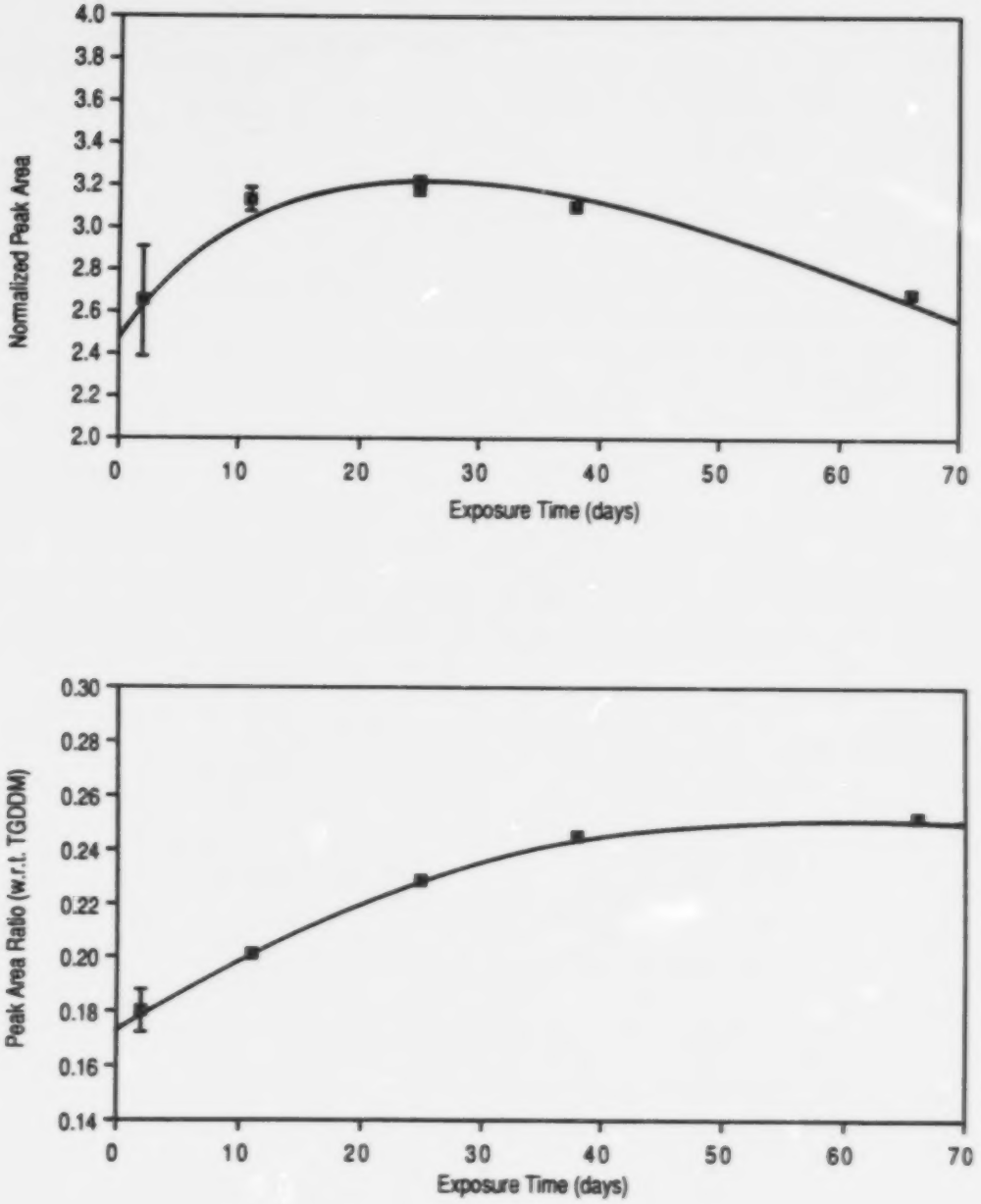


Figure 36. Variation of HS-RPLC peak 3 (TGDDM-DDS reaction product) as a function of prepreg exposure time.

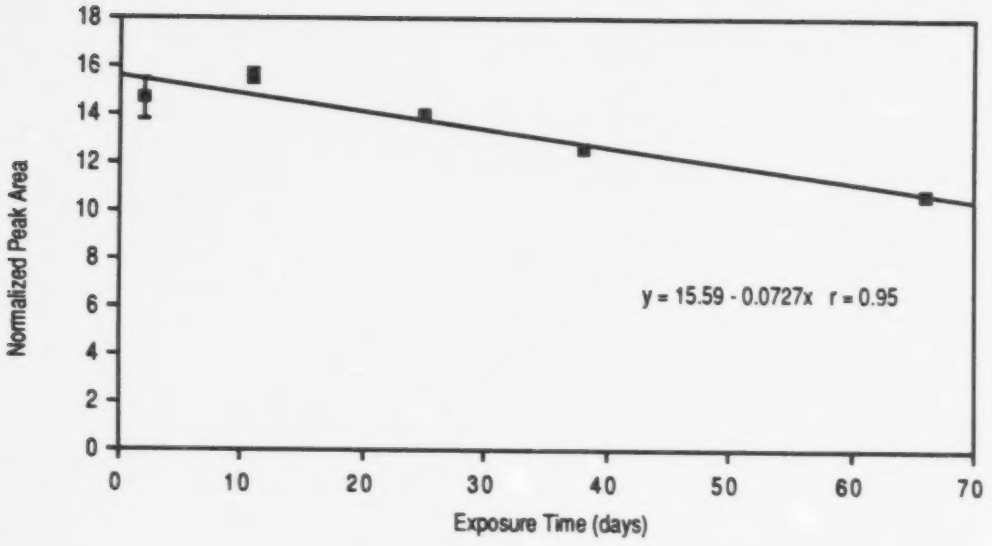


Figure 37. Variation of HS-RPLC peak 4 (TGDDM) as a function of prepreg exposure time.

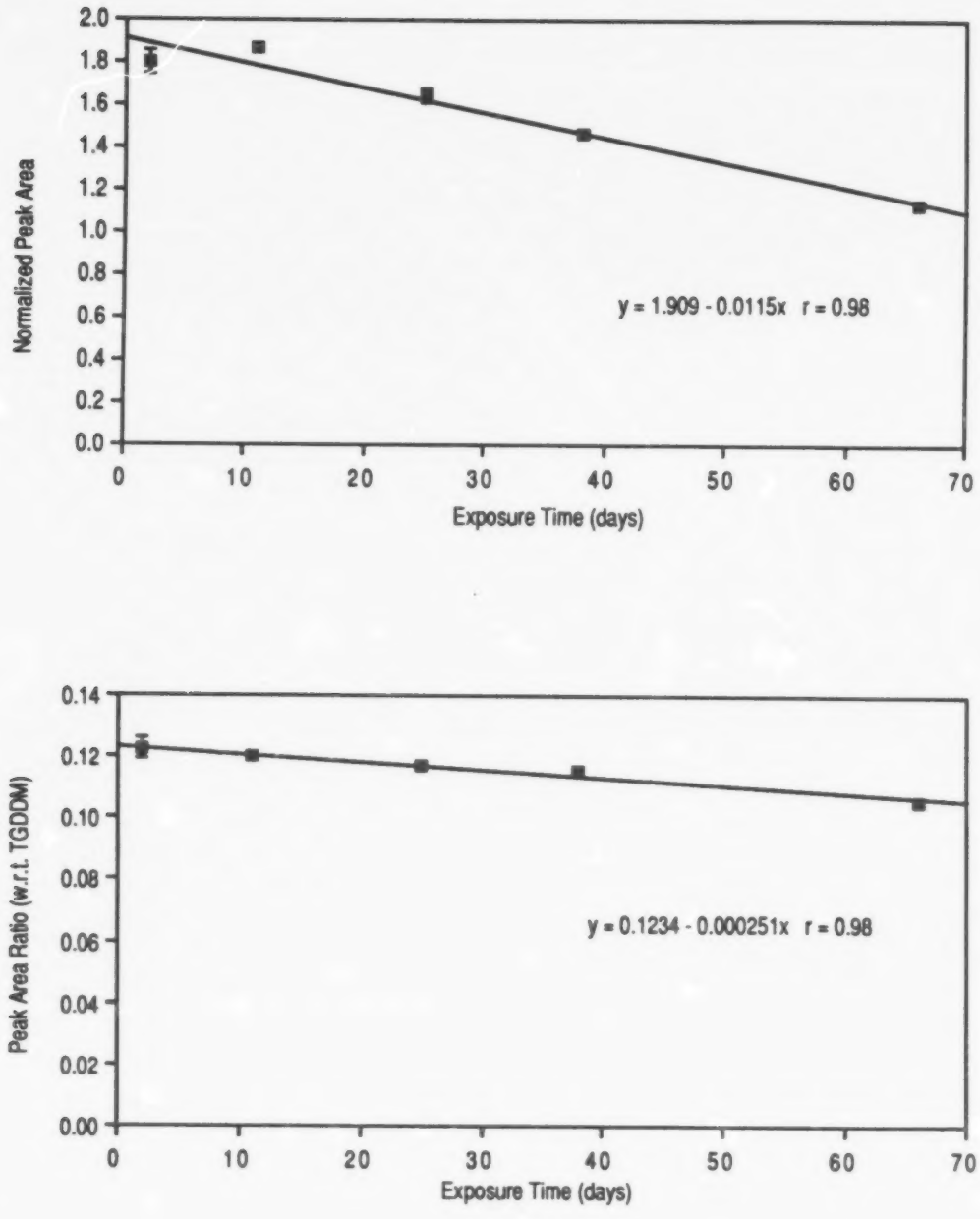


Figure 38. Variation of HS-RPLC peak 5 (DGEBA) as a function of prepreg exposure time.

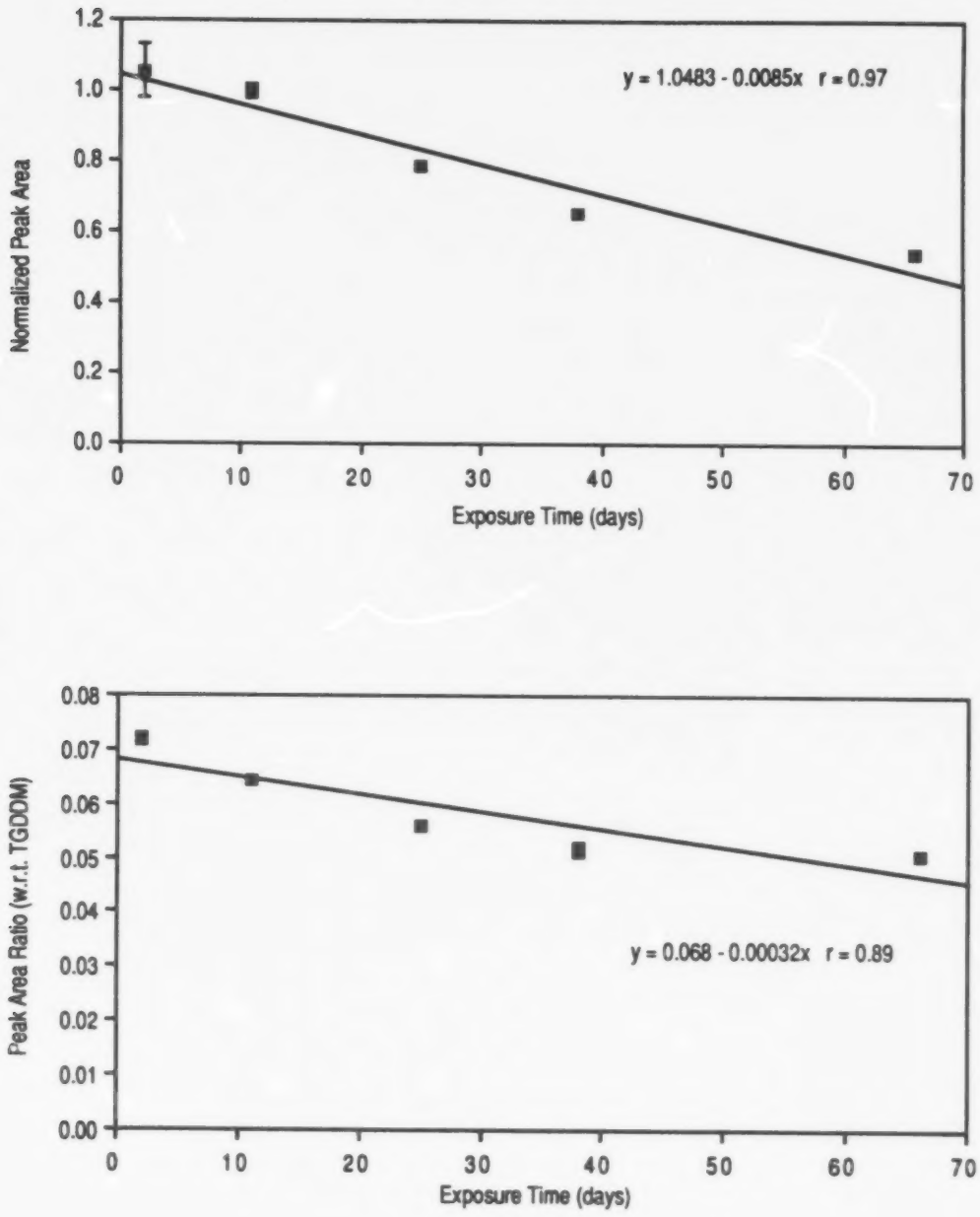

Normalized Peak Area
y = 1.0483 - 0.0085x r = 0.97
Exposure Time (days)
Peak Area Ratio (w.r.t. TGDDM)
y = 0.068 - 0.00032x r = 0.89
Exposure Time (days)

Figure 39. Variation of HS-RPLC peak 6 as a function of prepreg exposure time.

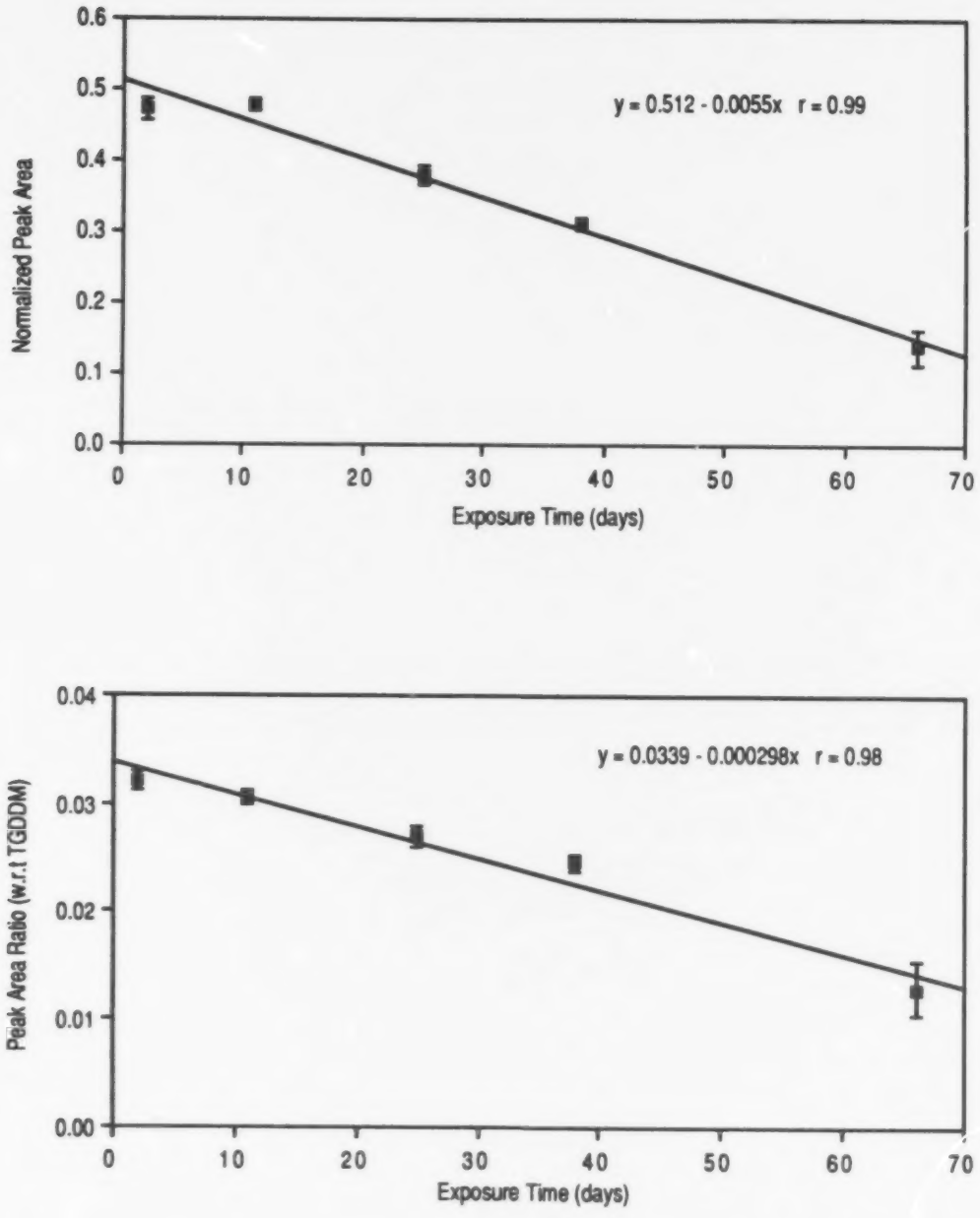

y = 0.512 - 0.0055x r = 0.99
Normalized Peak Area
Exposure Time (days)
y = 0.0339 - 0.000298x r = 0.98
Peak Area Ratio (w.r.t TGDDM)
Exposure Time (days)

Figure 40. Variation of HS-RPLC peak 7 as a function of prepreg exposure time.

Although the figures obtained in HS-RPLC are slightly different from those obtained in RPLC, they still show that the DGEBA disappears faster than the TGDDM. As in the previous case, the difference between the two methods may be due to the difference in resolution.

5.2.5 Peaks 6 and 7

For these peaks, whose origin is unknown, the variation is shown in Figures 39 and 40. Based on normalized peak area, the rates of decrease are 0.81% and 1.07% per day respectively, with very good correlation coefficients.

5.2.6 Discussion

The HS-RPLC results show that this technique can provide the same information as ordinary RPLC, but with significant savings in time and materials. The most useful parameters are the peaks of the hardener DDS (peak 1) and the TGDDM-DDS reaction product (peak 3). As in RPLC, the DDS peak is probably the best choice for monitoring the prepreg aging.

5.3 HIGH-PERFORMANCE SIZE-EXCLUSION CHROMATOGRAPHY

High-performance size-exclusion chromatography was performed as described in Section 2.3.3.6. A typical chromatogram is given in Figure 41. Peak areas were calculated with respect to vertical lines drawn from the valleys on either side of the peak to the overall baseline of the chromatogram. Since peaks 2 and 3 are not always well resolved, they were combined for the area calculation. Relative peak areas were obtained by dividing by the total area of the chromatogram. The solutions analysed were the same ones used for RPLC analysis (Section 5.1). Thus for each sample two THF extractions were done (A and B) and each solution was injected three times. The results are summarized in Table 9. In addition to the individual peak areas, a quantity labelled "degree of polymerization index" was also calculated. This is equal to the total area of peaks 1, 2, 3, and 4 (which correspond to products of higher molecular weight) divided by the sum of the areas of peaks 5 and 6 (which correspond mainly to the monomers DDS, TGDDM, and DGEBA). The variation of the different individual peaks and the "degree of polymerization index" as a function of the exposure time is shown graphically in Figures 42 to 47.

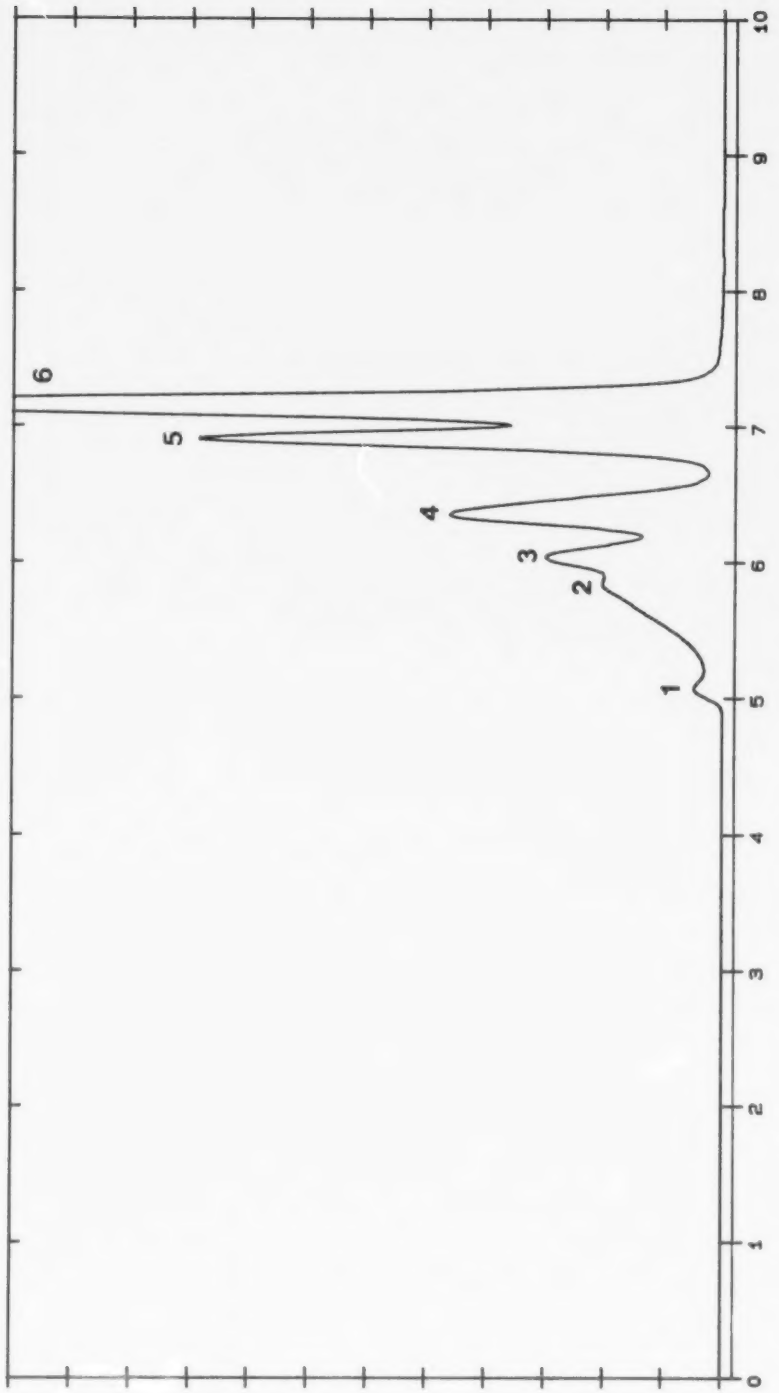


Figure 41: HPSEC chromatogram of Narmco 5208 prepreg (THF extract)

Table 9 (Part 1). HPSEC results (relative peak areas as % of total area)

Sample	Peak 1		Peak "2+3"		Peak 4	
	Value	SD	Value	SD	Value	SD
Control-A	3.163	0.018	13.7	3.5	16.15	0.26
Control-B	2.89	0.10	11.64	0.42	16.92	0.66
2-A	3.15	0.70	11.7	4.3	16.5	1.3
2-B	2.73	0.51	8.4	3.1	15.41	0.62
4-A	3.25	0.39	15.2	1.6	16.83	0.72
4-B	3.34	0.015	15.3	1.1	17.10	0.43
7-A	2.90	0.36	15.0	1.9	16.6	1.1
7-B	3.17	0.56	10.2	1.6	16.83	0.53
9-A	3.03	0.12	12.6	1.0	16.607	0.054
9-B	3.40	0.21	11.62	0.64	16.48	0.21
11-A	2.64	0.75	16.1	1.2	15.75	0.61
11-B	2.330	0.068	12.4	1.4	16.82	0.11
14-A	3.11	0.13	9.1	2.7	15.86	0.49
14-B	3.14	0.25	12.8	4.1	17.0	1.6
17-A	2.90	0.85	17.0	1.5	17.60	0.52
17-B	3.53	0.62	18.4	2.6	17.53	0.22
21-A	3.9		16.1		16.2	
21-B	7.19	0.38	21.60	0.96	16.6	1.8
25-A	3.71	0.90	19.5	4.2	17.68	0.32
25-B	2.7	1.5	18.6	4.8	19.1	1.9
29-A	3.09	0.93	18.6	2.3	19.6	1.2
29-B	2.2	1.4	18.6	1.3	20.11	0.22
32-A	3.49	0.21	16.13	0.63	17.702	0.012
32-B	3.28		22.131	0.041	16.32	0.28
35-A	5.3	1.1	25.4	1.4	17.28	0.56
35-B	3.7	0.43	21.2	1.5	17.371	0.084
38-B	4.73	0.52	20.3	7.7	17.1	1.1
42-A	5.6	0.46	25.60	0.12	16.48	0.15
42-B	4.06	0.74	22.1	3.9	17.55	0.12
45-A	5.21	0.16	17.6	6.0	17.0	1.0
45-B	6.6	1.5	27.4	5.6	17.5	1.4
52-A	7.45	0.39	27.31	0.88	17.1	2.0
52-B	8.0	1.7	30.4	1.9	17.5	2.4
59-A	9.03	0.35	33.33	0.18	16.41	0.17
59-B	7.99	0.21	33.31	0.70	16.45	0.35
66-A	10.7		24.2		12.0	
66-B	10.5	1.5	28.3	1.0	17.32	0.84
50D-A	4.86	0.98	22.8	6.3	18.5	2.3
50D-B	4.767	0.021	16.6	1.9	17.07	0.61
87F-A	3.13	0.15	10.9	2.0	16.8	1.7
87F-B	3.2		9.8		14.6	

Table 9 (Part 2). HPSEC results (relative peak areas as % of total area)

Sample	Peak 5		Peak 6		"Degree of polymerization index"
	Value	SD	Value	SD	
Control-A	25.44	0.67	43.1	2.3	0.482
Control-B	25.362	0.012	42.86	0.97	0.461
2-A	25.2	1.4	43.5	3.5	0.456
2-B	26.6	1.2	46.83	0.84	0.361
4-A	23.82	0.56	40.9	1.7	0.545
4-B	23.71	0.28	40.49	0.75	0.557
7-A	23.82	0.65	41.8	2.4	0.526
7-B	25.32	0.15	44.5	1.4	0.433
9-A	24.4	0.22	43.6	1.5	0.474
9-B	24.627	0.034	43.88	0.60	0.460
11-A	23.80	0.35	42.30	0.84	0.522
11-B	24.3	0.37	44.2	1.0	0.461
14-A	25.1	1.3	46.8	1.9	0.390
14-B	23.6	1.1	43.4	3.3	0.492
17-A	21.64	0.81	40.9	1.2	0.600
17-B	21.22	0.89	39.3	2.5	0.652
21-A	22.2		41.4		0.569
21-B	19.2	0.9	35.4	1.3	0.831
25-A	19.9	1.4	39.2	4.1	0.692
25-B	21.0	2.2	38.5	2.3	0.679
29-A	19.90	0.61	38.8	1.4	0.703
29-B	21.44	0.44	37.72	0.64	0.692
32-A	19.774	0.096	42.92	0.37	0.595
32-B	18.60	0.68	38.65	0.43	0.729
35-A	16.5	1.2	35.5	2.2	0.923
35-B	18.56	0.45	39.5	1.8	0.728
38-B	18.4	2.0	39.4	6.5	0.729
42-A	14.7	1.4	37.6	2.1	0.912
42-B	17.2	1.2	39.0	3.5	0.778
45-A	17.4	1.7	42.8	3.4	0.661
45-B	14.5	2.0	34.0	4.6	1.062
52-A	13.65	0.20	34.51	0.91	1.077
52-B	12.99	0.48	31.0	1.7	1.271
59-A	11.96	0.24	29.27	0.21	1.425
59-B	12.12	0.37	30.11	0.43	1.368
66-A	13.9		39.7		0.875
66-B	12.0	1.9	31.8	1.9	1.281
50D-A	16.3	2.2	37.5	3.8	0.446
50D-B	23.20	0.55	38.38	0.76	0.382
87F-A	25.07	0.44	44.08	0.30	0.858
87F-B	24.5		47.8		0.624

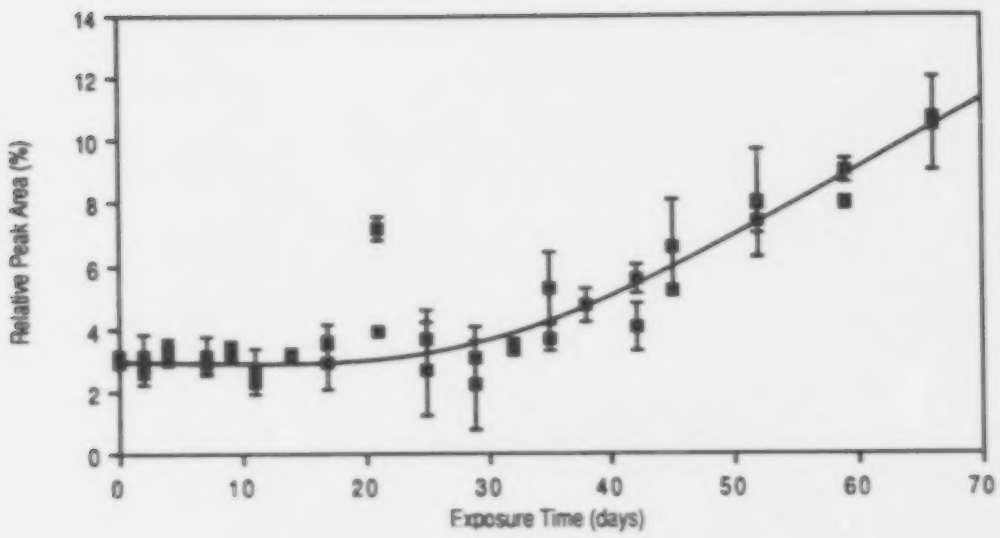


Figure 42. Variation of HPSEC peak 1 as a function of prepreg exposure time.

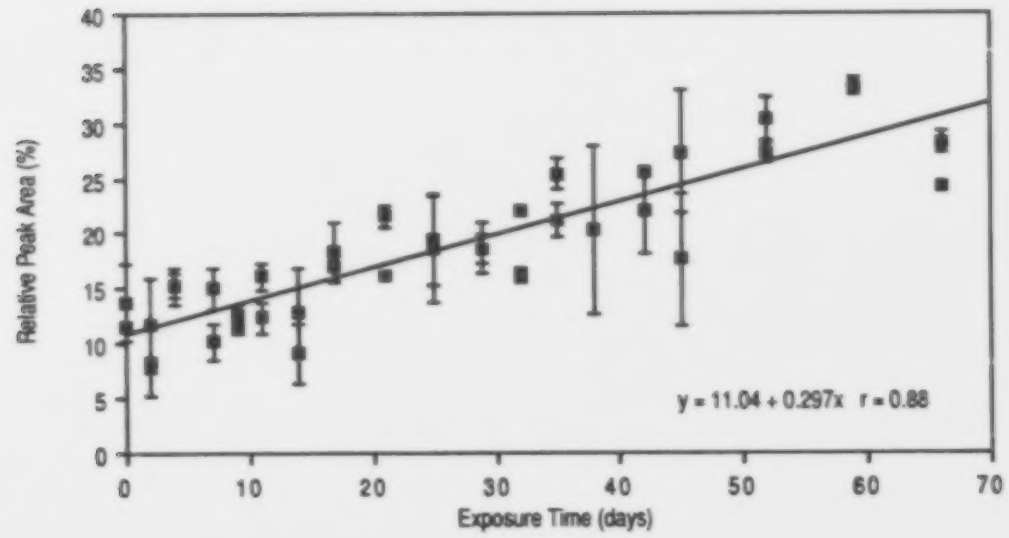


Figure 43. Variation of combined HPSEC peaks 2 and 3 as a function of prepreg exposure time.

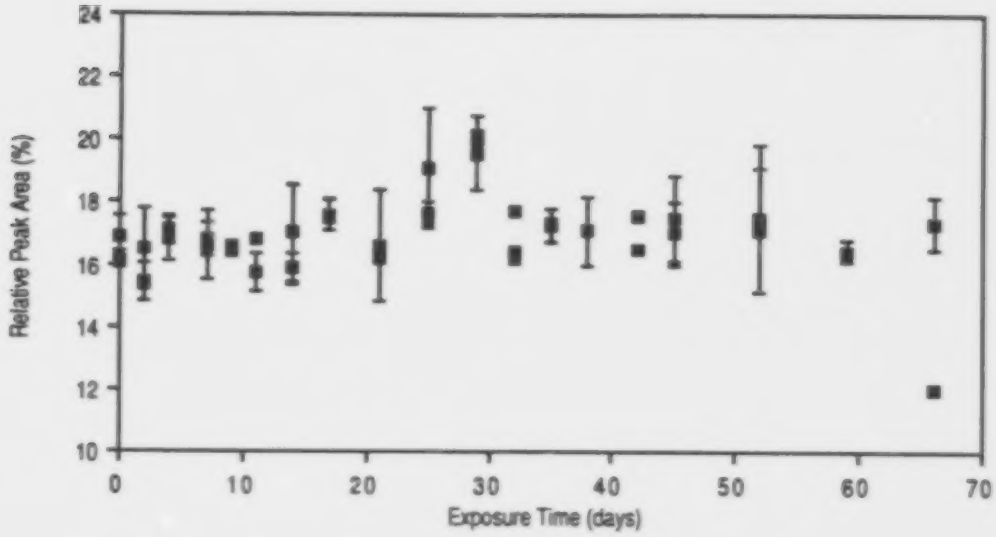


Figure 44. Variation of HPSEC peak 4 as a function of prepreg exposure time.

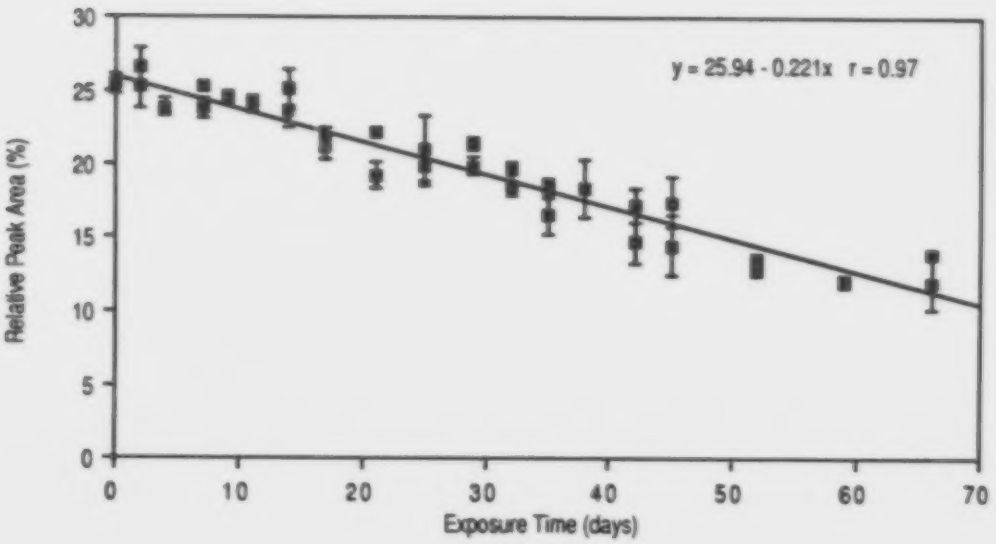


Figure 45. Variation of HPSEC peak 5 (DDS) as a function of prepreg exposure time.

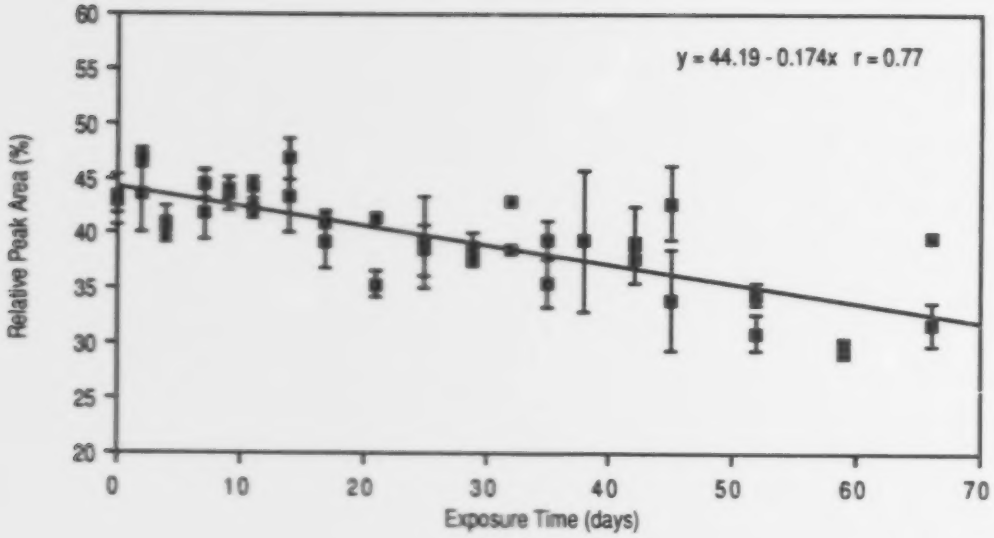


Figure 46. Variation of HPSEC peak 6 (TGDDM) as a function of prepreg exposure time.

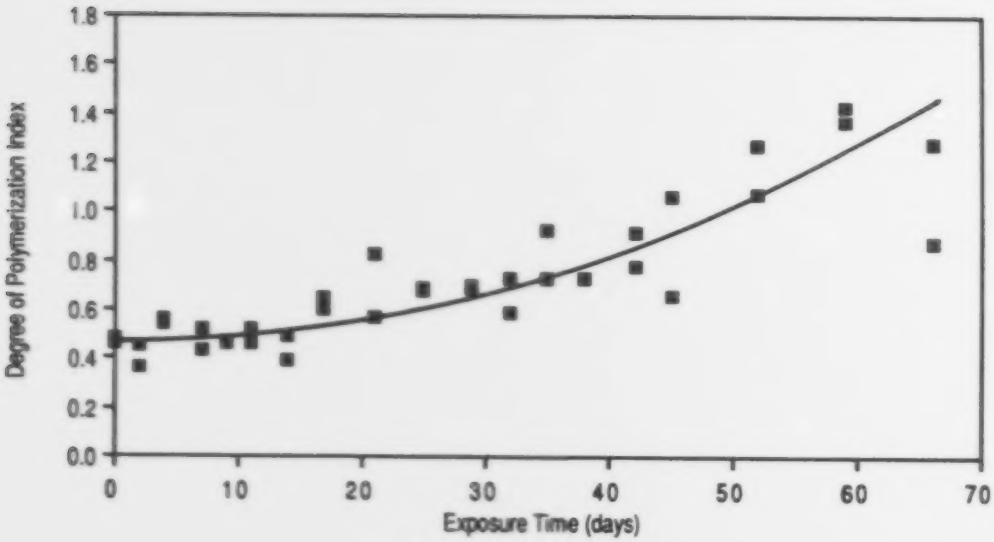


Figure 47. Variation of "degree of polymerization index" (as measured by HPSEC) as a function of prepreg exposure time.

5.3.1 Peak 1

Peak 1 corresponds to compounds of higher molecular weight. The exclusion limit for the column used is about 3500. Figure 42 shows that there is little change in the relative area before 30 days exposure, at which point there is a sharp increase. There is a peak at this position in the chromatogram of the Novolac resin believed to be present in the Narmco 5208. During the first 30 days, this epoxy species probably decreases due to reaction with amine, but at the same time new molecules of the same size are formed by reaction of smaller molecules. As a result, the overall size of this peak changes little until the Novolac species is consumed, at which point an increase is observed. It is interesting to note that the change in slope in Figure 42 occurs around the same time that a significant change is observed in the curves obtained for the TGDDM-DDS reaction product in RPLC or HS-RPLC.

5.3.2 Peaks "2+3" and 4

For the combined peaks 2 and 3, Figure 43 shows a steady increase in relative area, attributed to the expected formation of higher-molecular-weight components. However, there is a substantial degree of scatter, which is reflected in the relatively low correlation coefficient of 0.88 for the linear regression.

Peak 4 (Figure 44) remains fairly constant, no doubt for the same reasons as peak 1.

5.3.3 Peaks 5 and 6

As reported earlier [3], peaks 5 and 6 are related mainly to the monomers DDS and TGDDM respectively. Their variation is shown in Figures 45 and 46. They both show a steady decrease, much the same as observed in RPLC. As in that case, the DDS shows the most significant change. Linear regression for the relative peak area gives the following equation:

$$\text{Relative area (\%)} = 25.94 - 0.221 \times (\text{number of days exposure})$$

with a correlation coefficient of 0.97. This corresponds to a decrease of 0.85% per day, which is slightly lower than the figure of 1.02% found by RPLC. However, in RPLC the peak is well resolved and its intensity can be directly related to the amount of DDS present through the use of an internal standard. In HPSEC, the DDS peak involves contributions from other compounds which may not decrease with the aging; hence, the rate of decrease of the relative area is lower than in RPLC.

For the TGDDM, linear regression (Figure 46) gives a line corresponding to a decrease of 0.39% per day, compared to 0.38% as measured by RPLC.

5.3.4 Degree of polymerization index

The "degree of polymerization index" is plotted in Figure 47. There is a gradual linear increase over the first 40 days, followed by a more rapid increase beyond this point. This is about the same time at which the reaction product formed from TGDDM and DDS reaches its maximum level (Sections 5.1.2 and 5.2.2). It is the point at which the proportion of high-molecular-weight compounds (bigger than the TGDDM-DDS reaction product) becomes important.

5.3.5 Discussion

Crabtree and Hewitt [5,6] have monitored the aging of Narmco 5208 at 22°C by size-exclusion chromatography and obtained chromatograms which resemble those reported here, except that elution times were three times as long. The results were expressed quantitatively in terms of the ratios of certain pairs of peaks, and substantial changes (in the form of linear increases) were observed over a fifteen-day period. It is impossible to make a direct comparison with the results given here because ultraviolet detection was used rather than refractive index detection.

HPSEC is not as sensitive as RPLC for detecting variations among different batches, but it can be useful for following variations in the degree of advancement. The "degree of polymerization index" seems adequate for monitoring the sudden increase of high-molecular-weight species, but the peak of the hardener (DDS) is better for measuring the aging of the epoxy system.

6. PYROLYSIS - CAPILLARY GAS CHROMATOGRAPHY

This technique is briefly described in Section 2.3.3.7, and a typical pyrogram of the Narmco 5208 prepreg is shown in Figure 48. The quantitative results shown in Table 10 were obtained by taking the ratio of the areas of selected peaks in the chromatogram with respect to that of peak 2, the most intense peak, which corresponds to aniline. The values given are the average over three pyrograms.

Table 10. Pyrolysis - capillary gas chromatography results (peak area as % of aniline peak area).

Sample	Peak 1	Peak 3	Peak 4	Peak 7	Peak 8
Control	25.9	10.9	10.9	4.2	13.6
2	28.2	10.7	10.4	4.2	14.6
4	25.8	10.5	10.6	4.0	12.5
7	27.4	10.9	10.6	4.1	12.5
9	23.8	11.2	9.9	4.1	11.2
11	23.3	10.7	10.4	3.6	10.0
14	24.9	11.2	11.1	4.1	11.1
17	26.6	12.2	11.4	5.5	11.7
21	25.6	11.3	11.0	4.4	11.0
25	26.8	12.1	11.3	4.8	12.5
29	25.5	12.0	10.3	4.8	11.9
32	26.6	13.8	11.8	6.1	13.7
35	27.2	13.1	11.8	5.8	13.2
38	27.5	13.8	11.6	6.1	14.6
42	27.8	13.2	12.3	5.4	14.8
45	26.6	11.8	10.6	4.2	13.4
52	28.9	14.5	12.2	6.8	15.8
59	32.0	16.2	13.4	8.6	19.1
66	34.4	18.9	13.8	10.3	23.1

Figure 49 shows how the ratios vary with prepreg exposure time. In all cases, up to about 45 days there is no significant effect. Beyond this, a slight increase is observed. The fact that all the peaks show similar behaviour suggests that the real reason may be a decrease in the amount of aniline after 45 days. Generally speaking, this method is of little value for following the prepreg aging. This is not surprising, since aging simply changes the degree of polymerization of the resin, and pyrolysis results in "depolymerization". A better identification of all the major peaks could result in the finding of peaks which are specifically characteristic of higher-molecular-weight species. At the present time, the technique is of greater value for detecting variations in chemical composition, such as a change in the hardener/epoxy ratio [4].

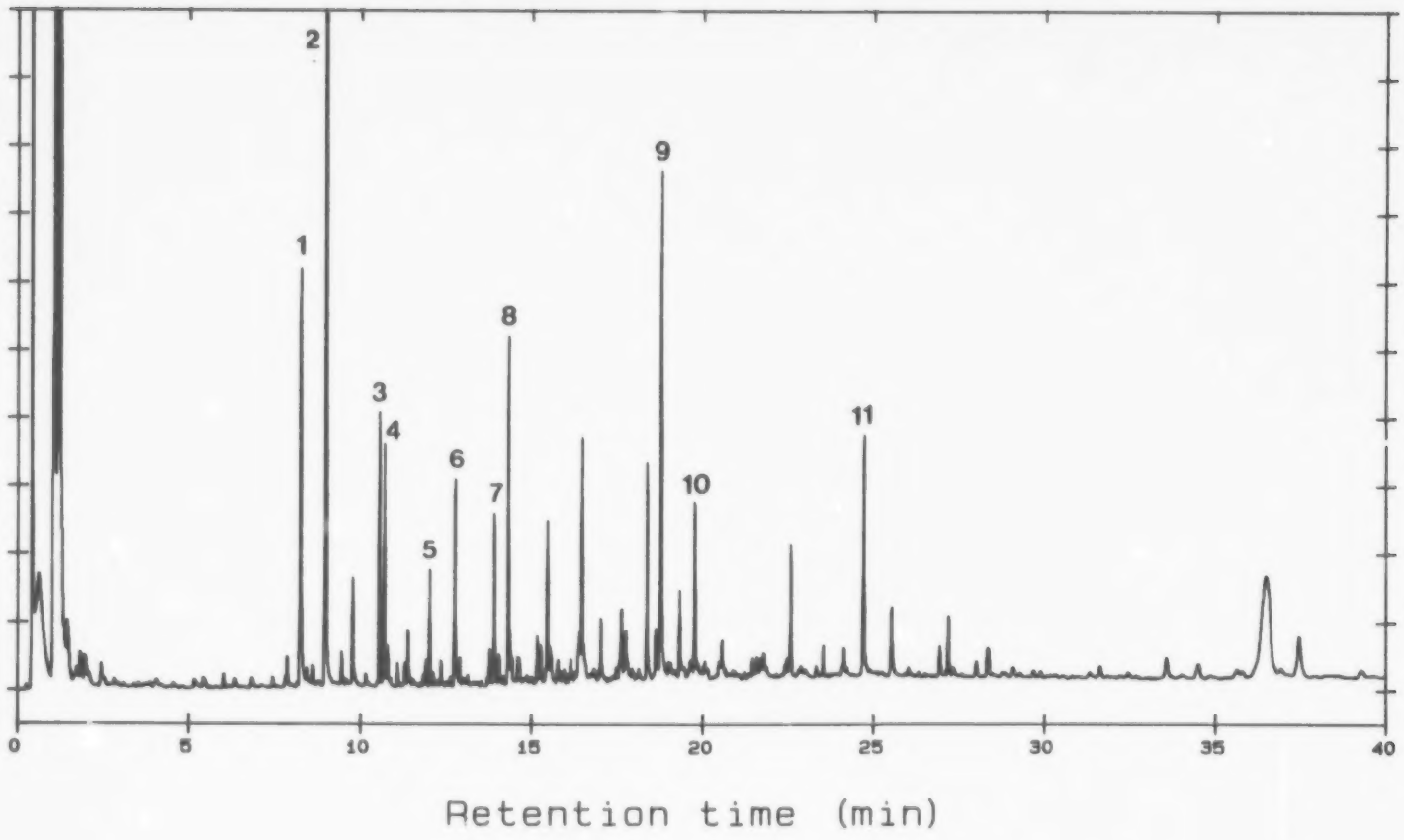


Figure 48: Pyrolysis - capillary gas chromatogram of Narmco 5208 prepreg.

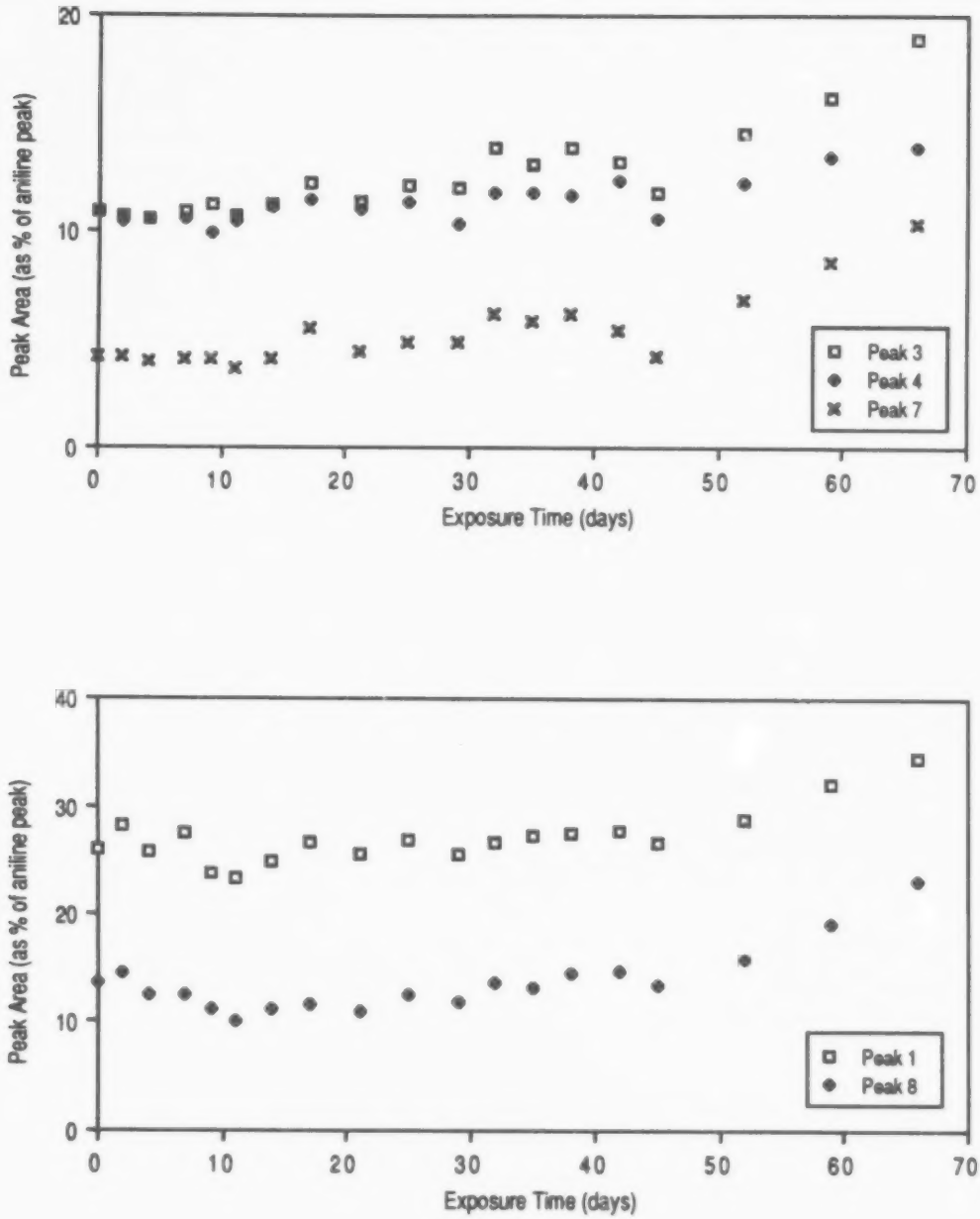


Figure 49. Variation of some peaks in the pyrolysis capillary gas chromatogram as a function of prepreg exposure time.

7. THERMAL ANALYSIS

Selected samples of aged prepreg were analysed by DSC as described in Section 2.3.3.8. For each sample, two to four specimens were measured. After the differential scanning calorimetry measurement, the exact weight of resin in the specimen used was determined by a thermogravimetric method described in Section 2.3.3.9. The results are summarized in Table 11.

Table 11. Thermal analysis results.

Sample	DSC wt. loss (%)	% Resin by wt.	ΔH (uncorrected) (J/g)	ΔH (corrected) (J/g)
Control	2.2	44.6	581	548
Control	1.2	40.0	525	552
Control	2.7	42.8	555	545
7	4.1	41.5	540	546
7	4.1	43.6	577	556
17	3.6	40.3	507	529
17	0.0	39.3	526	562
17	3.1	39.2	515	552
17	3.6	39.2	513	549
32	4.4	45.0	554	516
32	2.7	38.6	478	520
42	3.0	45.1	530	494
42	2.6	42.4	506	501
59	4.5	46.6	512	462
59	4.4	46.1	511	465
66	3.6	43.9	494	472
66	0.4	45.5	498	460
66	3.8	45.0	504	470
87F	4.4	44.1	586	558
87F	4.1	41.3	542	551

The second column gives the weight loss which occurs during the DSC measurement. As reported earlier [4], most of this occurs at higher temperatures. Up to 273°C, which is the upper limit for the integration of the DSC exotherm peak, the weight loss is less than 1% when nitrogen is used as atmosphere. Thus the measured value of ΔH is not significantly affected. However, in order to obtain a complete curve, the experiment is continued to 320°C, and since above 300°C the weight loss is not negligible, it must be combined with the TGA results in determining the total resin content. This is given in the third column. It is seen that it varies significantly from specimen to specimen. The values range from 38.6% to 46.6%, even though all specimens came from the same batch of prepreg.

To obtain meaningful values of the heat of polymerization, the area under the DSC peak must be divided by the weight of resin to give ΔH in joules per gram of resin. The fourth column of the table gives "uncorrected" values of ΔH, obtained by assuming that the resin weight is equal to 42% of the prepreg sample weight. (This figure corresponds to the nominal resin content of the prepreg.) The "uncorrected" values are plotted in Figure 50. While it can be seen that there is a gradual decrease with aging time, there is a large degree of scatter which would make it very difficult to accurately estimate the extent of aging by this method. The last column of the table gives the "corrected" ΔH values obtained by dividing by the true resin weight, as determined by TGA. When these values are plotted (Figure 51), the degree of scatter is much reduced. Linear regression gives a correlation coefficient of 0.95, as compared to 0.63 for the 'uncorrected" case. The equation obtained is:

$$\Delta H \text{ (J/g)} = 560.6 - 1.449 \times \text{(number of days exposure)}$$

This shows that ΔH, which is directly related to the number of unreacted epoxy groups in the resin, decreases by 0.26% per day from its initial value of 561 J/g. This is somewhat lower than the figure of 0.34% obtained by infrared spectroscopy (Section 4.1), which in theory is also related to the number of unreacted epoxy groups. One possible reason for the discrepancy is that two different epoxy resins are involved in the Narmco 5208 system, and the bisphenol A Novolac epoxy appears to react faster than the TGDDM-based one. If the two resins make different relative contributions to the IR epoxy index and the heat of polymerization, this may explain the difference between the results obtained by the two methods.

In spite of the reasonably good correlation obtained, DSC appears to be less sensitive than IR or RPLC for detecting small changes in composition, such as those which occur in the first 20 days of aging. It also requires considerably more time, because of the thermogravimetric analysis needed to obtain reproducible ΔH values.

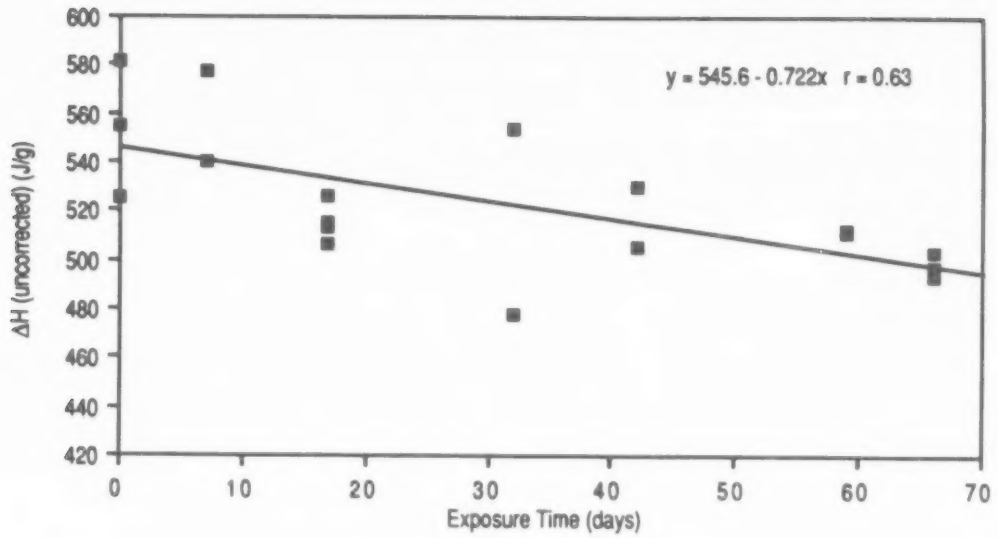


Figure 50. Variation of heat of polymerization ΔH (based on nominal resin content of 42%) as a function of prepreg exposure time.

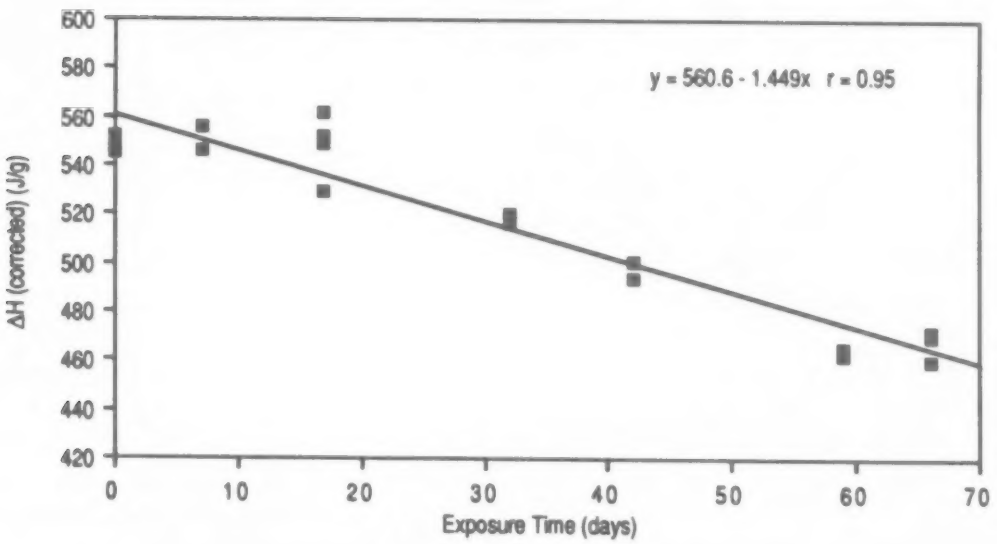


Figure 51. Variation of heat of polymerization ΔH (based on true resin content as measured by TGA) as a function of prepreg exposure time.

8. SPECIALLY AGED SAMPLES

As described in Section 2.1, in addition to the sheets of prepreg exposed at room temperature and 50% R.H., two other samples were tested. The first ("50D") was exposed for 50 days at room temperature, but in a dry atmosphere. The second ("87F") was stored in a freezer at -25°C and tested after 87 days. Results for these have been included in the tables previously given, but have not been discussed. The most important of these are given in Table 12, where they may be compared with results for the "Control" sample (0 days exposure) and two samples exposed at room temperature and 50% R.H. (35 days and 66 days).

The sample kept in the freezer is for all intents and purposes identical to the "Control" sample. No significant chemical changes are detectable. The only obvious difference is in the compressive properties, which appear to be rather low for the freezer-stored sample. However, this is not believed to be significant, statistically speaking, in view of the scatter observed for the compressive properties. More than one panel would have to be tested in order to confirm a significant difference.

The sample aged for 50 days under dry conditions gives results which in general indicate less resin advancement than a sample aged for the same time at 50% R.H. It is not possible to find a sample aged at 50% R.H. which exactly matches "50D", but the closest overall appears to be the one aged for 35 days, hence its inclusion in Table 12 for comparison purposes. Based on this, it can be concluded that in a dry atmosphere, resin advancement for Narmco 5208 occurs at about 70% of the rate at which it occurs in an atmosphere of 50% R.H. Thus humidity accelerates the polymerization reaction.

Table 12. Comparison of results for selected samples.

Exposure →	0	35	66	50D	87F
THF extraction (%)	43.1	42.8	43.9	42.8	42.7
Volatiles (%)	1.81	1.00	0.72	0.87	1.39
Resin flow (%)	26.2	26.1	24.6	--	26.5
Gel time (min)	21.0	15.3	7.2	--	20.9
Tensile strength (ksi)	92	91	93	--	100
Tensile modulus (Msi)	9.0	9.2	9.7	--	10.2
Ultimate strain (μin/in)	10640	10280	9650	--	9920
Comp. strength (ksi)	110	91	80	--	83
Comp. modulus (Msi)	9.8	9.9	9.5	--	9.6
Short beam shear (ksi)	11.1	7.2	7.7	--	6.9
IRT - ME Index [1]	0.409	0.355	0.332	0.352	0.398
IRT - MS Index [1]	1.055	1.069	1.076	1.087	1.039
RPLC - DDS [2]	3.993	2.345	1.335	2.351	4.037
RPLC - RP [2]	1.426	1.780	1.859	1.914	1.494
RPLC - TGDDM [2]	12.77	10.51	9.77	11.48	13.07
RPLC - DGEBA [2]	1.583	1.071	0.655	1.112	1.681
HPSEC - DPI [3]	0.472	0.826	1.078	0.741	0.414
DSC ΔH (corrected) (J/g)	548	--	467	--	554

[1] IRT = Infrared transmission, ME = multiple epoxy, MS = multiple sulphone

[2] RPLC = Reverse-phase liquid chromatography, peak areas w. r. t. acetophenone internal standard for DDS, RP (reaction product), TGDDM, and DGEBA

[3] DPI = "Degree of polymerization index" as determined by HPSEC (high-performance size-exclusion chromatography)

9. CONCLUSIONS

[1]. Significant chemical changes occur at a steady rate when prepreg containing Narmco 5208 resin is exposed to the atmosphere at room temperature (22°C) and 50% relative humidity for a period of 66 days. These changes can be detected with varying degrees of sensitivity by several physicochemical techniques. The physical properties of the prepreg are affected, and there is evidence that certain mechanical properties of cured panels prepared from the prepreg are also affected to some extent.

[2]. The results of the mechanical testing of cured panels show a high degree of scatter. When statistical methods (linear regression) are applied, the tensile properties (strength, modulus, ultimate strain) show no significant correlation with the prepreg exposure time. On the other hand, the compressive properties (strength and modulus) and the short-beam shear strength show evidence of a gradual decrease with prepreg aging time, of the order of 0.2% to 0.4% per day. The observed behaviour is not surprising, since tensile properties are determined largely by the fibres, whereas compressive and interlaminar shear properties are more dependent on the resin. Athough the changes appear to be small and possibly insignificant, it must be remembered that they are based on measurements of simple panels prepared in a laboratory under ideal conditions. For more complex parts made in a factory environment, and exposed to adverse conditions and stress over a long period of time, the effects could well be very much amplified.

[3]. The physical properties most affected by the aging are tack, volatiles content, and gel time. The volatiles content, initially at 1.9%, drops rapidly during the first few days, levelling off at 0.8%. The drop is due to loss of acetone, and is accompanied by a loss of tack. The residual volatiles content is attributed to moisture. Over 66 days, the gel time decreases substantially, from 21 minutes to 7.2 minutes. The resin flow does not change significantly over the period monitored.

[4]. The best parameters for following the chemical changes which take place are the following:

(i) The "epoxy index" as determined by infrared spectroscopy [2], either in transmission or in attenuated total reflection. This is an indicator of the number of unreacted epoxy groups present; it decreases by 0.34% per day from its initial value under the conditions studied.

(ii) The content of unreacted hardener DDS, as measured by reverse-phase high-performance liquid chromatography [3]. It decreases by 1.02% per day. It can also be monitored (with somewhat poorer precision) by high-performance size-exclusion chromatography.

(iii) The content of TGDDM-DDS reaction product, or the RP/TGDDM ratio, as measured by RPLC. These parameters are only suitable in the initial stages of aging, because after a certain time (30 days in the present case), they stop increasing.

[5]. The following parameters are also affected by the aging, but are less suitable than those just described because of greater experimental error in their determination:

(i) The heat of polymerization ΔH of the resin, as determined by differential scanning calorimetry. It decreases by 0.26% per day. In order to obtain reproducible values of ΔH, the resin content of each specimen of prepreg analysed must be determined by thermogravimetric analysis.

(ii) The content of TGDDM monomer, as measured by RPLC. This decreases by 0.38% per day.

(iii) The content of DGEBA monomer, as measured by RPLC. This decreases by 0.87% per day.

(iv) The "degree of polymerization index" as determined by high-performance size-exclusion chromatography. This shows a gradual increase up to about 40 days, then a more rapid increase beyond this point.

(v) Certain other peaks found in the RPLC and HPSEC chromatograms.

(vi) The ratios of certain peaks found in the pyrolysis - gas chromatogram. Significant changes are observed only after 40 days exposure time, so this method is not really of much practical use.

[6]. Prepreg exposed at room temperature but in a dry atmosphere changes somewhat more slowly (by a factor of about 0.7) than prepreg exposed at 50% R.H.

[7]. Prepreg stored in a freezer at -25°C for the duration of the experiment (66 days) showed no detectable signs of change.

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11. APPENDIX A

RPLC results for peak 1 (DDS).

Sample	Normalized area (w.r.t. ACP)		Normalized height (w.r.t. ACP)		Area ratio (w.r.t. TGDDM)		Height ratio (w.r.t. TGDDM)	
	Value	SD	Value	SD	Value	SD	Value	SD
Control-A	4.083	0.026	6.09	0.12	0.3145	0.0015	0.5475	0.0064
Control-B	3.9038	0.0034	5.851	0.020	0.3110	0.0010	0.5430	0.0050
2-A	3.9598	0.0079	7.28	0.23	0.30346	0.00088	0.593	0.023
2-B	4.016	0.013	7.282	0.026	0.30599	0.00042	0.5801	0.0078
4-A	3.743	0.020	7.84	0.56	0.2941	0.0018	0.634	0.058
4-B	3.8302	0.0098	7.658	0.020	0.29655	0.00059	0.6132	0.0025
7-A	3.695	0.011	6.903	0.023	0.2884	0.0014	0.574	0.033
7-B	3.7368	0.0079	7.10	0.13	0.2918	0.0021	0.5690	0.0032
9-A	3.551	0.071	7.352	0.096	0.2954	0.0022	0.616	0.025
9-B	3.584	0.091	7.49	0.11	0.3022	0.0091	0.605	0.011
11-A	3.456	0.016	6.853	0.032	0.28867	0.00062	0.5511	0.0094
11-B	3.457	0.014	7.41	0.22	0.28924	0.00085	0.601	0.020
14-A	3.576	0.042	6.88	0.19	0.2865	0.0023	0.542	0.016
14-B	3.613	0.044	6.96	0.11	0.2878	0.0030	0.5516	0.0053
17-A	3.36	0.10	5.61	0.68	0.27175	0.00074	0.506	0.062
17-B	3.370	0.038	6.93	0.27	0.2704	0.0036	0.589	0.035
21-A	3.395	0.029	6.39	0.18	0.2689	0.0018	0.500	0.013
21-B	3.381	0.025	6.528	0.066	0.2664	0.0012	0.5143	0.0051
25-A	3.1645	0.0090	6.19	0.39	0.25507	0.00010	0.496	0.026
25-B	3.153	0.019	6.013	0.032	0.25565	0.00018	0.4755	0.0075
29-A	2.952	0.026	5.845	0.060	0.24598	0.00049	0.4746	0.0045
29-B	2.971	0.014	5.71	0.10	0.2482	0.0015	0.4709	0.0040
32-A	2.693	0.043	5.123	0.036	0.23412	0.00022	0.4469	0.0078
32-B	2.789	0.028	5.212	0.022	0.24041	0.00062	0.4493	0.0076
35-A	2.3160	0.0035	4.83	0.12	0.22006	0.00092	0.4422	0.0097
35-B	2.3738	0.0085	4.823	0.095	0.22611	0.00056	0.439	0.010
38-A	2.219	0.012	4.682	0.058	0.21794	0.00024	0.4342	0.0038
38-B	2.280	0.014	4.816	0.071	0.2224	0.0019	0.444	0.011
42-A	1.998	0.055	3.758	0.064	0.1896	0.0018	0.3564	0.0053
42-B	2.115	0.021	3.99	0.11	0.1987	0.0017	0.3677	0.0071
45-A	1.951	0.040	3.827	0.088	0.1831	0.0018	0.372	0.011
45-B	2.0944	0.0089	4.118	0.080	0.19469	0.00087	0.398	0.011
52-A	1.821	0.057	3.488	0.063	0.1774	0.0014	0.3464	0.0054
52-B	1.789	0.061	3.38	0.10	0.17343	0.00010	0.3383	0.0031
59-A	1.6023	0.0096	2.899	0.037	0.15960	0.00038	0.2782	0.0025
59-B	1.673	0.020	2.939	0.083	0.15851	0.00034	0.2666	0.0052
66-A	1.445	0.012	2.441	0.016	0.1383	0.0023	0.2446	0.0017
66-B	1.224	0.016	2.315	0.058	0.1348	0.0012	0.240	0.011
50D-A	2.351	0.038	4.346	0.062	0.20480	0.00016	0.3972	0.0061
50D-B	4.0418	0.0054	7.50	0.80	0.3044	0.0013	0.575	0.071
87F-A	3.98	0.12	7.537	0.058	0.30958	0.00080	0.5647	0.0069
87F-B	4.093	0.062	7.398	0.092	0.3087	0.0026	0.537	0.020

APPENDIX A (contd.)

RPLC results for peak 7 (TGDDM-DDS Reaction Product)

Sample	Normalized area (w.r.t. ACP)		Normalized height (w.r.t. ACP)		Area ratio (w.r.t. TGDDM)		Height ratio (w.r.t. TGDDM)	
	Value	SD	Value	SD	Value	SD	Value	SD
Control-A	1.4363	0.0057	1.2329	0.0060	0.11063	0.00015	0.1108	0.0015
Control-B	1.4158	0.0016	1.214	0.013	0.11279	0.00033	0.1126	0.0018
2-A	1.5188	0.0019	1.2864	0.0056	0.11640	0.00015	0.1048	0.0017
2-B	1.4894	0.0027	1.2755	0.0092	0.11347	0.00008	0.1016	0.0022
4-A	1.588	0.035	1.332	0.046	0.1247	0.0027	0.1075	0.0018
4-B	1.5907	0.0040	1.3513	0.0063	0.12316	0.00030	0.10820	0.00093
7-A	1.6010	0.0061	1.368	0.016	0.1249	0.0010	0.1138	0.0052
7-B	1.5991	0.0033	1.3890	0.0058	0.12487	0.00092	0.1113	0.0019
9-A	1.552	0.026	1.351	0.028	0.1291	0.0014	0.1131	0.0018
9-B	1.562	0.052	1.4027	0.0024	0.1316	0.0044	0.1134	0.0035
11-A	1.5906	0.0049	1.4541	0.0096	0.13286	0.00026	0.1169	0.0020
11-B	1.5767	0.0081	1.443	0.011	0.13192	0.00055	0.11695	0.00083
14-A	1.745	0.021	1.540	0.024	0.1398	0.0016	0.1213	0.0019
14-B	1.826	0.018	1.536	0.014	0.14552	0.00028	0.1217	0.0024
17-A	1.753	0.065	1.5615	0.0022	0.14192	0.00075	0.1408	0.0016
17-B	1.7641	0.0067	1.522	0.018	0.14154	0.00097	0.1294	0.0032
21-A	2.0240	0.0021	1.691	0.012	0.16032	0.00097	0.1324	0.0013
21-B	1.9754	0.0053	1.712	0.030	0.15563	0.00022	0.1349	0.0012
25-A	2.007	0.059	1.662	0.039	0.1618	0.0052	0.1333	0.0044
25-B	2.070	0.010	1.719	0.032	0.16782	0.00027	0.1360	0.0025
29-A	2.050	0.054	1.721	0.012	0.1708	0.0058	0.1398	0.0016
29-B	2.0732	0.0051	1.704	0.018	0.17318	0.00068	0.1406	0.0019
32-A	1.991	0.072	1.699	0.027	0.1732	0.0081	0.1482	0.0037
32-B	2.001	0.092	1.662	0.011	0.1725	0.0069	0.1433	0.0027
35-A	1.7958	0.0038	1.675	0.015	0.17063	0.00012	0.1533	0.0023
35-B	1.7650	0.0022	1.6348	0.0069	0.16812	0.00021	0.1487	0.0020
38-A	1.7732	0.0062	1.6530	0.0029	0.17415	0.00017	0.1533	0.0021
38-B	1.770	0.014	1.6687	0.0048	0.1726	0.0012	0.1539	0.0026
42-A	1.868	0.038	1.6801	0.0096	0.17730	0.00017	0.1594	0.0018
42-B	1.8738	0.0023	1.712	0.014	0.17599	0.00024	0.1580	0.0028
45-A	1.868	0.039	1.619	0.023	0.17531	0.00021	0.1572	0.0020
45-B	1.85964	0.00018	1.633	0.021	0.17286	0.00005	0.1578	0.0029
52-A	1.823	0.060	1.634	0.015	0.17753	0.00043	0.1623	0.0026
52-B	1.827	0.065	1.609	0.020	0.17707	0.00024	0.1609	0.0030
59-A	1.767	0.012	1.591	0.028	0.17597	0.00002	0.1527	0.0049
59-B	1.872	0.043	1.5634	0.0090	0.17733	0.00016	0.1418	0.0021
66-A	2.0570	0.0098	1.493	0.031	0.19688	0.00076	0.1496	0.0052
66-B	1.66	0.14	1.411	0.050	0.183	0.012	0.1479	0.0038
50D-A	1.914	0.011	1.6641	0.0098	0.1668	0.0019	0.1521	0.0024
50D-B	1.5198	0.0123	1.25	0.12	0.11446	0.00057	0.096	0.011
87F-A	1.458	0.043	1.276	0.010	0.11326	0.00037	0.09564	0.00093
87F-B	1.529	0.019	1.3462	0.0002	0.11533	0.00067	0.0977	0.0023

APPENDIX A (contd.)

RPLC results for peak 8

Sample	Normalized area (w.r.t. ACP)		Normalized height (w.r.t. ACP)		Area ratio (w.r.t. TGDDM)		Height ratio (w.r.t. TGDDM)	
	Value	SD	Value	SD	Value	SD	Value	SD
Control-A	1.1360	0.0028	0.5606	0.0084	0.08750	0.00025	0.05037	0.00083
Control-B	1.0895	0.0073	0.5292	0.0054	0.08680	0.00044	0.04912	0.00085
2-A	0.96	0.14	0.6372	0.0095	0.073	0.011	0.05191	0.00086
2-B	1.0387	0.0030	0.6485	0.0076	0.07913	0.00005	0.05166	0.00061
4-A	0.7619	0.0048	0.639	0.015	0.05986	0.00010	0.05162	0.00059
4-B	0.7768	0.0012	0.6429	0.0048	0.06015	0.00012	0.05148	0.00060
7-A	0.724	0.044	0.617	0.029	0.0565	0.0036	0.05120	0.00055
7-B	0.7632	0.0073	0.6504	0.0041	0.05960	0.00093	0.05211	0.00043
9-A	0.83	0.17	0.608	0.029	0.069	0.012	0.05090	0.00078
9-B	0.938	0.141	0.627	0.017	0.079	0.012	0.05067	0.00033
11-A	0.82	0.19	0.6207	0.0030	0.068	0.016	0.04990	0.00045
11-B	0.93	0.19	0.6078	0.0075	0.078	0.016	0.04927	0.00029
14-A	0.7187	0.0077	0.6420	0.0091	0.05758	0.00073	0.0501	0.0013
14-B	0.7351	0.0077	0.6448	0.0078	0.05857	0.00015	0.05109	0.00050
17-A	0.624	0.017	0.576	0.013	0.0506	0.0022	0.0520	0.0011
17-B	0.7181	0.0081	0.606	0.013	0.05762	0.00084	0.05152	0.00008
21-A	0.7364	0.0028	0.6644	0.0089	0.05833	0.00053	0.05203	0.00070
21-B	0.7111	0.0046	0.6545	0.0040	0.05602	0.00050	0.05157	0.00065
25-A	0.714	0.014	0.6474	0.0079	0.0576	0.0013	0.05189	0.00037
25-B	0.708	0.013	0.650	0.010	0.05741	0.00069	0.05139	0.00017
29-A	0.6843	0.0040	0.6410	0.0026	0.05701	0.00068	0.05204	0.00049
29-B	0.6875	0.0014	0.6317	0.0021	0.05743	0.00004	0.05212	0.00066
32-A	0.6491	0.0090	0.5998	0.0073	0.05644	0.00019	0.05231	0.00019
32-B	0.6516	0.0053	0.598	0.012	0.05616	0.00025	0.05159	0.00048
35-A	0.4586	0.0096	0.5496	0.0060	0.04357	0.00081	0.05031	0.00051
35-B	0.5255	0.0089	0.5471	0.0079	0.05005	0.00086	0.0498	0.0010
38-A	0.4077	0.0034	0.5459	0.0053	0.04004	0.00015	0.05063	0.00055
38-B			0.5551	0.0019			0.05933	0.00067
42-A	0.581	0.014	0.5620	0.0067	0.05516	0.00019	0.05331	0.00097
42-B	0.5912	0.0041	0.5873	0.0041	0.05553	0.00049	0.05418	0.00056
45-A	0.599	0.011	0.5468	0.0021	0.05623	0.00026	0.05308	0.00014
45-B	0.6040	0.0034	0.5539	0.0062	0.05614	0.00033	0.05351	0.00079
52-A	0.566	0.016	0.5376	0.0044	0.05511	0.00034	0.05340	0.00091
52-B	0.585	0.018	0.545	0.011	0.05670	0.00017	0.05450	0.00062
59-A	0.579	0.018	0.578	0.011	0.0569	0.0011	0.0554	0.0012
59-B	0.600	0.014	0.5962	0.0099	0.05686	0.00049	0.05409	0.00041
66-A	0.6154	0.0016	0.5574	0.0028	0.05890	0.00066	0.0559	0.0010
66-B	0.522	0.015	0.5192	0.0062	0.05750	0.00054	0.0560	0.0011
50D-A	0.6424	0.0033	0.5759	0.0046	0.05598	0.00069	0.05264	0.00090
50D-B	0.98	0.14	0.6676	0.0023	0.074	0.011	0.05110	0.00079
87F-A	0.782	0.019	0.686	0.012	0.06077	0.00012	0.05144	0.00050
87F-B	0.8000	0.0093	0.718	0.022	0.0603	0.0011	0.05207	0.00042

APPENDIX A (contd.)

RPLC results for peak 9 (TGDDM)

Sample	Normalized area (w.r.t. ACP)		Normalized height (w.r.t. ACP)	
	Value	SD	Value	SD
Control-A	12.982	0.066	11.13	0.10
Control-B	12.552	0.040	10.777	0.081
2-A	13.049	0.034	12.27	0.15
2-B	12.126	0.031	12.55	0.18
4-A	12.727	0.063	12.39	0.24
4-B	12.9160	0.0086	12.489	0.064
7-A	12.815	0.055	12.05	0.67
7-B	12.807	0.084	12.48	0.18
9-A	12.05	0.33	11.94	0.41
9-B	12.07	0.33	12.38	0.37
11-A	11.972	0.046	12.44	0.16
11-B	11.952	0.048	12.34	0.12
14-A	12.482	0.086	12.71	0.40
14-B	12.551	0.010	12.62	0.15
17-A	12.35	0.39	11.09	0.11
17-B	12.464	0.042	11.77	0.259
21-A	12.630	0.088	12.77	0.015
21-B	12.693	0.048	12.69	0.16
25-A	12.406	0.040	12.48	0.18
25-B	12.334	0.082	12.65	0.18
29-A	12.003	0.095	12.317	0.065
29-B	11.972	0.018	12.12	0.12
32-A	11.50	0.18	11.46	0.16
32-B	11.601	0.095	11.60	0.19
35-A	10.524	0.028	10.925	0.074
35-B	10.498	0.012	10.99	0.19
38-A	10.182	0.046	10.78	0.14
38-B	10.252	0.034	10.90	0.19
42-A	10.54	0.21	10.544	0.087
42-B	10.647	0.021	10.84	0.12
45-A	10.66	0.22	10.302	0.064
45-B	10.76	0.0022	10.35	0.12
52-A	10.27	0.36	10.07	0.25
52-B	10.32	0.35	10.00	0.31
59-A	10.038	0.057	10.42	0.15
59-B	10.56	0.15	11.023	0.098
66-A	10.448	0.090	9.98	0.14
66-B	9.09	0.18	9.41	0.23
50D-A	11.48	0.19	10.94	0.22
50D-B	13.278	0.073	13.06	0.23
87F-A	12.87	0.34	13.35	0.16
87F-B	13.260	0.090	13.79	0.32

APPENDIX A (contd.)

RPLC results for peak 10

Sample	Normalized area (w.r.t. ACP)		Normalized height (w.r.t. ACP)		Area ratio (w.r.t. TGDDM)		Height ratio (w.r.t. TGDDM)	
	Value	SD	Value	SD	Value	SD	Value	SD
Control-A	1.6773	0.0099	1.703	0.021	0.12920	0.00029	0.15299	0.00061
Control-B	1.48906	0.00050	1.490	0.021	0.11863	0.00035	0.1383	0.0012
2-A	1.4503	0.0042	1.779	0.011	0.11114	0.00010	0.1449	0.0017
2-B	1.49616	0.00075	1.859	0.012	0.11399	0.00032	0.1481	0.0015
4-A	1.462	0.014	1.874	0.018	0.11487	0.00082	0.1512	0.0017
4-B	1.4550	0.0024	1.848	0.017	0.11265	0.00025	0.14802	0.00066
7-A	1.496	0.033	1.870	0.053	0.1167	0.0028	0.1553	0 0044
7-B	1.473	0.020	1.870	0.024	0.11503	0.00079	0.14983	0.00072
9-A	1.374	0.014	1.724	0.011	0.1143	0.0019	0.1444	0.0042
9-B	1.420	0.037	1.728	0.042	0.1198	0.0041	0.13962	0.00077
11-A	1.3563	0.0062	1.627	0.016	0.11329	0.00015	0.13083	0.00042
11-B	1.3769	0.0038	1.661	0.012	0.11520	0.00015	0.13464	0.00069
14-A	1.526	0.053	1.868	0.055	0.1222	0.0034	0.1470	0.0023
14-B	1.3820	0.0072	1.823	0.044	0.11012	0.00049	0.1445	0.0018
17-A	1.335	0.079	1.435	0.022	0.1080	0.0030	0.1294	0.0021
17-B	1.363	0.0085	1.659	0.069	0.10938	0.00046	0.1409	0.0039
21-A	1.3754	0.0072	1.739	0.036	0.10894	0.00043	0.1362	0.0014
21-B	1.4124	0.0081	1.778	0.024	0.11127	0.00047	0.14002	0.00018
25-A	1.305	0.014	1.616	0.034	0.1052	0.0012	0.1295	0.0012
25-B	1.3341	0.0088	1.6696	0.0097	0.10816	0.00000	0.1320	0.0016
29-A	1.221	0.012	1.556	0.014	0.10170	0.00025	0.12633	0.00066
29-B	1.2861	0.0066	1.623	0.038	0.10743	0.00040	0.1339	0.0018
32-A	1.100	0.020	1.433	0.023	0.09562	0.00023	0.12495	0.00052
32-B	1.167	0.010	1.505	0.015	0.10057	0.00034	0.12978	0.00095
35-A	1.0509	0.0011	1.2693	0.0047	0.09986	0.00035	0.11618	0.00076
35-B	1.0919	0.0020	1.329	0.022	0.10401	0.00027	0.12088	0.00023
38-A	0.963	0.013	1.209	0.018	0.09460	0.00085	0.1121	0.0013
38-B	0.9662	0.0077	1.201	0.010	0.09425	0.00049	0.11073	0.00060
42-A	0.918	0.091	1.155	0.031	0.0870	0.0068	0.1096	0.0027
42-B	0.951	0.053	1.225	0.016	0.0894	0.0051	0.11305	0.00026
45-A	0.934	0.069	1.118	0.027	0.0876	0.0047	0.1086	0.0027
45-B	0.9243	0.0011	1.145	0.010	0.08592	0.00005	0.11061	0.00082
52-A	0.829	0.090	1.049	0.046	0.0806	0.0058	0.1041	0.0025
52-B	0.828	0.037	1.023	0.050	0.0802	0.0056	0.1022	0.0023
59-A	0.7757	0.0095	1.0083	0.0093	0.07702	0.00060	0.09675	0.00075
59-B	0.826	0.010	1.0401	0.0060	0.0782	0.0013	0.09437	0.00030
66-A	0.712	0.043	0.806	0.030	0.0682	0.0047	0.0808	0.0019
66-B	0.598	0.040	0.747	0.016	0.0658	0.0033	0.0782	0.0022
50D-A	1.112	0.031	1.298	0.029	0.0969	0.0013	0.11867	0.00030
50D-B	1.515	0.012	1.916	0.080	0.11408	0.00038	0.1468	0.0084
87F-A	1.610	0.042	2.114	0.021	0.12505	0.00004	0.15839	0.00078
87F-B	1.751	0.051	2.268	0.086	0.1321	0.0030	0.1645	0.0024

APPENDIX A (contd.)

RPLC results for peak 11

Sample	Normalized area (w.r.t. ACP)		Normalized height (w.r.t. ACP)		Area ratio (w.r.t. TGDDM)		Height ratio (w.r.t. TGDDM)	
	Value	SD	Value	SD	Value	SD	Value	SD
Control-A	1.2273	0.0082	0.532	0.011	0.09453	0.00072	0.0575	0.0083
Control-B	1.185	0.016	0.6612	0.0074	0.0944	0.0016	0.06136	0.00075
2-A	1.212	0.010	0.637	0.011	0.09285	0.00057	0.0519	0.0010
2-B	1.2226	0.0036	0.6581	0.0085	0.09314	0.00019	0.0524	0.0014
4-A	0.85	0.27	0.607	0.010	0.067	0.021	0.04901	0.00064
4-B	0.7146	0.0094	0.610	0.017	0.05532	0.00071	0.0488	0.0015
7-A	0.85	0.27	0.576	0.034	0.066	0.021	0.0480	0.0050
7-B	0.85	0.26	0.608	0.014	0.066	0.020	0.0487	0.0015
9-A	1.01	0.24	0.589	0.013	0.084	0.020	0.0493	0.0028
9-B	1.141	0.067	0.587	0.018	0.0962	0.0058	0.0474	0.0028
11-A	1.122	0.046	0.612	0.024	0.09374	0.00368	0.0492	0.0018
11-B	1.106	0.016	0.601	0.011	0.0925	0.0011	0.04869	0.00053
14-A	0.675	0.065	0.591	0.057	0.0541	0.0050	0.0464	0.0030
14-B	0.6280	0.0033	0.575	0.012	0.05004	0.00064	0.0456	0.0010
17-A	0.92	0.24	0.536	0.065	0.074	0.017	0.0505	0.0024
17-B	0.616	0.019	0.530	0.019	0.0494	0.0014	0.04506	0.00065
21-A	0.513	0.017	0.507	0.010	0.0406	0.0014	0.0397	0.0011
21-B	0.527	0.052	0.490	0.013	0.04084	0.0018	0.03856	0.00055
25-A	0.486	0.033	0.451	0.023	0.03715	0.00040	0.0361	0.0017
25-B	0.440	0.026	0.463	0.021	0.0357	0.0019	0.0366	0.0016
29-A	0.431	0.034	0.4428	0.0038	0.0359	0.0026	0.03595	0.00057
29-B	0.411	0.030	0.434	0.013	0.0343	0.0026	0.0358	0.0014
32-A	0.4270	0.0028	0.4165	0.0077	0.03714	0.00043	0.03632	0.00017
32-B	0.4289	0.0089	0.4147	0.0072	0.03697	0.00059	0.03575	0.00026
35-A	0.4746	0.0094	0.4111	0.0028	0.0451	0.0010	0.03763	0.00044
35-B	0.521	0.048	0.440	0.037	0.0496	0.0046	0.04002	0.00038
38-A	0.406	0.055	0.393	0.052	0.0398	0.0052	0.0364	0.0049
38-B	0.3492	0.0084	0.400	0.012	0.03406	0.00072	0.03098	0.00093
42-A	0.321	0.015	0.319	0.011	0.0305	0.0014	0.03027	0.00078
42-B	0.356	0.018	0.3623	0.0062	0.0334	0.0016	0.03343	0.00021
45-A	0.3148	0.0040	0.3138	0.0038	0.02954	0.00035	0.03046	0.00025
45-B	0.3275	0.0077	0.334	0.012	0.03044	0.00072	0.03223	0.00097
52-A	0.305	0.023	0.318	0.016	0.0297	0.0012	0.0316	0.0015
52-B	0.290	0.024	0.313	0.011	0.0280	0.0015	0.03134	0.00014
59-A	0.2901	0.0307	0.294	0.022	0.02722	0.00001	0.0282	0.0021
59-B	0.295	0.016	0.271	0.011	0.0280	0.0011	0.02462	0.00077
66-A	0.2822	0.0056	0.2998	0.0021	0.0270	0.0031	0.03005	0.00020
66-B	0.248	0.020	0.2584	0.0086	0.0274	0.0028	0.0260	0.0028
50D-A	0.3797	0.0074	0.381	0.012	0.03725	0.00007	0.03478	0.00043
50D-B	1.07	0.30	0.626	0.067	0.081	0.023	0.0480	0.0059
87F-A	0.753	0.024	0.673	0.016	0.05848	0.00028	0.05039	0.00089
87F-B	0.777	0.022	0.700	0.031	0.0586	0.0013	0.0507	0.0011

APPENDIX A (contd.)

RPLC results for peak 14

Sample	Normalized area (w.r.t. ACP)		Normalized height (w.r.t. ACP)		Area ratio (w.r.t. TGDDM)		Height ratio (w.r.t. TGDDM)	
	Value	SD	Value	SD	Value	SD	Value	SD
Control-A	0.6614	0.0100	0.4140	0.0023	0.05095	0.00054	0.03720	0.00052
Control-B	0.3526	0.0075	0.3586	0.0071	0.02809	0.00062	0.03327	0.00081
2-A	0.400	0.032	0.4030	0.0068	0.0307	0.0026	0.03284	0.00092
2-B	0.4309	0.0061	0.4196	0.0051	0.03283	0.00046	0.03343	0.00090
4-A	0.4134	0.0033	0.4279	0.0041	0.03248	0.00041	0.0345	0.0010
4-B	0.4184	0.0024	0.4200	0.0054	0.03239	0.00018	0.03363	0.00041
7-A	0.431	0.014	0.440	0.019	0.03360	0.00096	0.0367	0.0037
7-B	0.4180	0.0014	0.426	0.0041	0.03264	0.00033	0.03414	0.00061
9-A	0.43	0.13	0.4091	0.0092	0.0356	0.0094	0.03426	0.00086
9-B	0.3672	0.0060	0.4260	0.0058	0.03100	0.00049	0.0344	0.0015
11-A	0.3225	0.0041	0.4093	0.0012	0.02694	0.00044	0.03291	0.00051
11-B	0.3263	0.0047	0.4220	0.0083	0.02730	0.00029	0.03421	0.00060
14-A	0.390	0.013	0.472	0.013	0.0313	0.0011	0.03714	0.00016
14-B	0.38378	0.00039	0.4156	0.0078	0.03058	0.00026	0.0329	0.0010
17-A	0.528	0.023	0.355	0.011	0.04277	0.00074	0.0320	0.0013
17-B	0.403	0.014	0.396	0.013	0.0323	0.0012	0.03361	0.00073
21-A	0.5593	0.0071	0.4252	0.0034	0.04430	0.00037	0.03330	0.00012
21-B	0.4107	0.0068	0.4361	0.0055	0.03236	0.00044	0.03436	0.00078
25-A	0.424	0.082	0.3948	0.0078	0.0342	0.0067	0.03164	0.00064
25-B	0.5290	0.0022	0.4027	0.0057	0.04289	0.00047	0.03185	0.00002
29-A	0.452	0.074	0.3865	0.0037	0.0377	0.0064	0.03138	0.00025
29-B	0.5170	0.0098	0.4070	0.0098	0.04319	0.00075	0.03358	0.00058
32-A	0.3304	0.0088	0.3458	0.0043	0.02873	0.00055	0.03017	0.00079
32-B	0.3414	0.0015	0.3646	0.0083	0.02943	0.00030	0.03143	0.00035
35-A	0.4127	0.0068	0.3353	0.0045	0.03921	0.00076	0.03069	0.00057
35-B	0.4227	0.0044	0.3430	0.0042	0.04026	0.00037	0.03120	0.00023
38-A	0.330	0.070	0.3132	0.0042	0.03239	0.00676	0.02905	0.00068
38-B	0.416	0.057	0.3138	0.0029	0.04062	0.00056	0.02894	0.00067
42-A	0.261	0.041	0.286	0.012	0.0249	0.0044	0.0272	0.0012
42-B	0.315	0.059	0.3034	0.0040	0.0296	0.0056	0.02800	0.00064
45-A	0.256	0.042	0.278	0.011	0.0241	0.0041	0.0270	0.0013
45-B	0.2963	0.0012	0.2921	0.0042	0.02754	0.00012	0.02822	0.00060
52-A	0.286	0.069	0.2655	0.0055	0.0277	0.0056	0.02637	0.00074
52-B	0.259	0.016	0.2578	0.0032	0.0251	0.0010	0.02578	0.00058
59-A	0.3566	0.0224	0.285	0.014	0.0344	0.0011	0.0274	0.0018
59-B	0.3565	0.0036	0.2760	0.0048	0.03378	0.00082	0.02504	0.00066
66-A	0.2651	0.0039	0.2196	0.0013	0.02537	0.00015	0.02200	0.00017
66-B	0.142	0.081	0.185	0.034	0.0155	0.0085	0.0129	0.0111
50D-A	0.3309	0.0141	0.3075	0.0065	0.02883	0.00099	0.02810	0.00006
50D-B	0.4417	0.0067	0.423	0.040	0.03327	0.00054	0.0324	0.0036
87F-A	0.452	0.011	0.4962	0.0056	0.03513	0.00012	0.03718	0.00068
87F-B	0.47744	0.00094	0.5592	0.0055	0.03601	0.00032	0.04057	0.00054

APPENDIX A (contd.)

RPLC results for peak 15

Sample	Normalized area (w.r.t. ACP)		Normalized height (w.r.t. ACP)		Area ratio (w.r.t. TGDDM)		Height ratio (w.r.t. TGDDM)	
	Value	SD	Value	SD	Value	SD	Value	SD
Control-A	0.1688	0.0056	0.1904	0.0036	0.01300	0.00004	0.01711	0.00016
Control-B	0.1436	0.0017	0.1576	0.0032	0.01144	0.00013	0.01462	0.00022
2-A	0.0894	0.0020	0.1627	0.0012	0.00685	0.00014	0.01325	0.00024
2-B	0.09125	0.00083	0.1707	0.0016	0.00695	0.00007	0.01360	0.00007
4-A	0.09364	0.00038	0.1793	0.0020	0.00736	0.00007	0.01447	0.00044
4-B	0.0903	0.0035	0.1756	0.0020	0.00699	0.00027	0.01406	0.00009
7-A	0.0989	0.0015	0.1871	0.0015	0.00772	0.00008	0.01556	0.00077
7-B	0.09262	0.00026	0.1759	0.0025	0.00723	0.00007	0.01409	0.00003
9-A	0.0858	0.0018	0.1627	0.0032	0.00713	0.00007	0.01363	0.00021
9-B	0.0606	0.0467	0.1688	0.0040	0.0051	0.0039	0.01364	0.00010
11-A	0.08314	0.00064	0.1637	0.0017	0.00694	0.00007	0.01316	0.00007
11-B	0.08623	0.00032	0.1727	0.0021	0.00721	0.00000	0.01400	0.00016
14-A	0.0936	0.0015	0.1852	0.0016	0.00750	0.00009	0.01458	0.00034
14-B	0.08165	0.00036	0.1584	0.0029	0.00651	0.00006	0.01255	0.00017
17-A	0.07098	0.00057	0.1292	0.0027	0.0058	0.00017	0.01165	0.00014
17-B	0.0824	0.0024	0.1508	0.0051	0.00661	0.00021	0.01282	0.00020
21-A	0.13697	0.00040	0.1765	0.0076	0.01085	0.00009	0.01382	0.00051
21-B	0.08366	0.00084	0.1638	0.0040	0.00659	0.00005	0.01291	0.00031
25-A	0.093	0.030	0.153	0.010	0.0075	0.0024	0.01222	0.00070
25-B	0.011	0.036	0.1680	0.0097	0.0087	0.0029	0.0092	0.0079
29-A	0.086	0.028	0.1384	0.0065	0.0072	0.0024	0.01123	0.00048
29-B	0.103	0.030	0.154	0.010	0.0086	0.0025	0.01269	0.0079
32-A	0.0660	0.0020	0.1211	0.0038	0.00574	0.00010	0.01056	0.00019
32-B	0.0694	0.0014	0.1357	0.0033	0.00598	0.00005	0.01169	0.00009
35-A	0.06408	0.00049	0.1246	0.0048	0.00609	0.00006	0.01140	0.00036
35-B	0.077	0.018	0.1347	0.0098	0.0074	0.0018	0.01224	0.00069
38-A	0.073	0.018	0.1236	0.0064	0.0072	0.0017	0.01146	0.00053
38-B	0.066	0.011	0.1178	0.0056	0.0064	0.0011	0.01086	0.00039
42-A	0.0550	0.0025	0.1085	0.0017	0.00521	0.00013	0.01029	0.00016
42-B	0.071	0.013	0.1180	0.0047	0.0067	0.0012	0.01089	0.00041
45-A	0.05424	0.00069	0.1054	0.0033	0.00509	0.00006	0.01023	0.00030
45-B	0.05628	0.00043	0.1091	0.0014	0.00523	0.00004	0.01054	0.00011
52-A	0.0516	0.0037	0.0991	0.0068	0.00503	0.00045	0.00984	0.00061
52-B	0.0504	0.0017	0.0956	0.0043	0.00489	0.00001	0.00956	0.00014
59-A	0.0563	0.0154	0.1008	0.0057	0.00474	0.00003	0.00968	0.00058
59-B	0.04954	0.00031	0.09181	0.00046	0.00469	0.00004	0.00833	0.00003
66-A	0.075	0.015	0.0834	0.0031	0.0072	0.0014	0.00836	0.00020
66-B	0.0542	0.0021	0.0424	0.0033	0.00597	0.00026	0.00784	0.00047
50D-A	0.06264	0.00084	0.1145	0.0019	0.00546	0.00015	0.01046	0.00007
50D-B	0.09729	0.00091	0.172	0.015	0.00733	0.00004	0.0132	0.0013
87F-A	0.0999	0.0014	0.2051	0.0054	0.0088	0.0013	0.01536	0.00024
87F-B	0.1095	0.0026	0.2311	0.0089	0.00826	0.00014	0.01676	0.00026

APPENDIX A (contd.)

RPLC results for peak 16

Sample	Normalized area (w.r.t. ACP)		Normalized height (w.r.t. ACP)		Area ratio (w.r.t. TGDDM)		Height ratio (w.r.t. TGDDM)	
	Value	SD	Value	SD	Value	SD	Value	SD
Control-A	0.1270	0.0014	0.1405	0.0015	0.00978	0.00015	0.01262	0.00013
Control-B	0.11013	0.00064	0.1177	0.0020	0.00877	0.00006	0.01092	0.00015
2-A	0.11145	0.00073	0.12761	0.00001	0.00845	0.00004	0.01040	0.00013
2-B	0.1133	0.0014	0.1321	0.0014	0.00863	0.00012	0.01052	0.00009
4-A	0.1128	0.0019	0.1357	0.0020	0.00886	0.00017	0.01095	0.00027
4-B	0.1086	0.0039	0.1316	0.0022	0.00841	0.00030	0.01054	0.00012
7-A	0.1141	0.0022	0.13795	0.00091	0.00891	0.00014	0.01148	0.00072
7-B	0.1107	0.0013	0.1309	0.0018	0.00846	0.00016	0.01049	0.00005
9-A	0.10079	0.00094	0.1221	0.0026	0.00838	0.00019	0.01022	0.00016
9-B	0.1031	0.0015	0.12555	0.00067	0.00869	0.00016	0.01015	0.00028
11-A	0.0950	0.0026	0.1220	0.0016	0.00794	0.00019	0.00981	0.00004
11-B	0.09964	0.00029	0.1288	0.0017	0.00834	0.00002	0.01044	0.00016
14-A	0.096	0.011	0.1329	0.0049	0.00766	0.00090	0.01046	0.00039
14-B	0.09948	0.00082	0.1199	0.0012	0.00793	0.00012	0.00950	0.00008
17-A	0.0957	0.0036	0.1113	0.0040	0.00775	0.00009	0.01004	0.00040
17-B	0.1015	0.0015	0.1206	0.0030	0.00814	0.00013	0.01025	0.00008
21-A	0.0946	0.0012	0.1211	0.0035	0.00749	0.00007	0.00948	0.00026
21-B	0.07859	0.00067	0.1237	0.0048	0.00619	0.00003	0.00975	0.00031
25-A	0.076	0.095	0.1076	0.0039	0.00614	0.00078	0.00862	0.00026
25-B	0.08950	0.00050	0.11780	0.00017	0.00726	0.00001	0.0062	0.0054
29-A	0.0725	0.0083	0.1006	0.0019	0.00604	0.00073	0.00817	0.00018
29-B	0.0874	0.0015	0.1136	0.0041	0.00730	0.00012	0.00937	0.00025
32-A	0.0672	0.0024	0.0902	0.0017	0.00585	0.00019	0.00787	0.00064
32-B	0.0630	0.0075	0.0957	0.0018	0.00543	0.00060	0.00825	0.00026
35-A	0.06391	0.00018	0.09292	0.00079	0.00607	0.00003	0.00851	0.00012
35-B	0.06777	0.00070	0.0967	0.0020	0.00646	0.00007	0.00880	0.00012
38-A	0.05832	0.00010	0.08553	0.00048	0.00573	0.00002	0.00793	0.00012
38-B	0.05841	0.00021	0.096	0.021	0.00570	0.00005	0.0089	0.0019
42-A	0.0403	0.0043	0.0718	0.0021	0.00382	0.00034	0.00681	0.00021
42-B	0.0430	0.0011	0.0775	0.0014	0.00404	0.00011	0.00715	0.00020
45-A	0.0390	0.0014	0.07052	0.00089	0.00366	0.00021	0.00684	0.00011
45-B	0.0416	0.0043	0.0736	0.0012	0.00387	0.00040	0.00713	0.00023
52-A	0.03528	0.00049	0.0639	0.0020	0.00344	0.00007	0.00635	0.00013
52-B	0.0348	0.0018	0.0623	0.0072	0.00337	0.00023	0.00623	0.00017
59-A	0.03443	0.00075	0.0617	0.0013	0.00340	0.00003	0.00592	0.00007
59-B	0.03503	0.00006	0.06080	0.00032	0.00332	0.00004	0.00552	0.00008
66-A	0.0306	0.0048	0.0494	0.0025	0.00293	0.00048	0.00495	0.00018
66-B	0.02373	0.00097	0.0300	0.0028	0.00261	0.00014	0.00457	0.00022
50D-A	0.0508	0.0026	0.0802	0.0044	0.00442	0.00016	0.00733	0.00027
50D-B	0.11592	0.00018	0.131	0.014	0.00873	0.00005	0.0100	0.0012
87F-A	0.1256	0.0019	0.1580	0.0013	0.00976	0.00011	0.01184	0.00014
87F-B	0.1381	0.0040	0.1820	0.0072	0.01042	0.00023	0.01320	0.00022